GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: February 23, 1976

Project Title: Chemistry of Carbanions

Project No: G-33-610

Principal Investigator Dr. E. Grovenstein, Jr.

Sponsor: National Science Foundation

Agreement Period: From 1/1/76 Until 6/30/77*

*12 months budget period plus 6 months for submission of required reports, etc.

Type Agreement: Grant No. CHE76-02720

Amount: $35,000 NSF (G-33-610)
7,462 GIT (G-33-358)
$42,462 Total

Reports Required:

Final Report; Annual Letter Technical Report if project continued.

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RA-3 (9-75)

2-58187172

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 7/15/82

Project Title: Chemistry of Carbanions

Project No: G-33-610

Project Director: Dr. E. Grovenstein, Jr.

Sponsor: NSF

Effective Termination Date: 6/30/80

Clearance of Accounting Charges: 9/30/80

Grant/Contract Closeout Actions Remaining:

- [x] Final Invoice and Closing Documents
- [ ] Final Fiscal Report
- [x] Final Report of Inventions
- [x] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Assigned to: Chemistry (School/Laboratory)

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FORM OCA 10/78]

Carbanions. XVIII. Spiro Anions from Reactions of 2- and 3-p-Biphenylylalkyl Chlorides with Cs-K-Na Alloy

J. A. Bertrand, Erling Grovenstein, Jr., Pang-chia Lu, and Don VanDerveer

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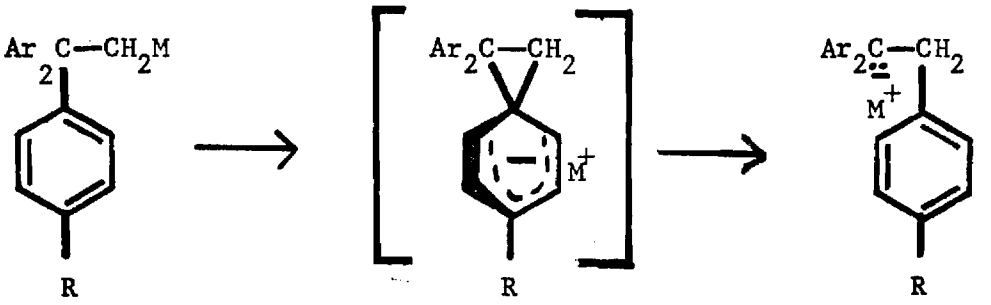
Abstract: 3-Chloro-1-p-biphenylylpropane reacts with Cs-K-Na alloy in tetrahydrofuran (THF) at -75° to give organoalkali compounds which upon carbonation after one minute afford 36% yield (based on starting chloride) of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid (8), 14% of p-biphenylylacetic acid, 3% of 2-p-biphenylylbutanoic acid, and 6% of 4-p-biphenylylbutanoic acid. The spiro anionic precursor of 8 has a half-life of about 13 minutes under the reaction conditions cited. 3-Chloro-2-p-biphenylyl-2,3-dimethylbutane with Cs-K-Na alloy under similar reaction conditions gives after carbonation 28% yield of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (11) and 7% of 3-p-biphenylyl-2,2,3-trimethylbutanoic acid. Under the reaction conditions the spiro anionic precursor of 11 has a half-life of about 22 minutes. The structures of the reacting chlorides and the product carboxylic acids are assigned based on their analytical and spectroscopic properties. In addition the structure of 11 is confirmed by single-crystal x-ray diffraction analysis.

Carbanions. XVIII. Spiro Anions from Reactions of 2- and 3-p-Biphenylylalkyl Chlorides with Cs-K-Na Alloy

Sir:

Spiro anions (1) have long been suggested as intermediates or transition states[1] in [1,2] migrations of aryl groups in organoalkali compounds. That



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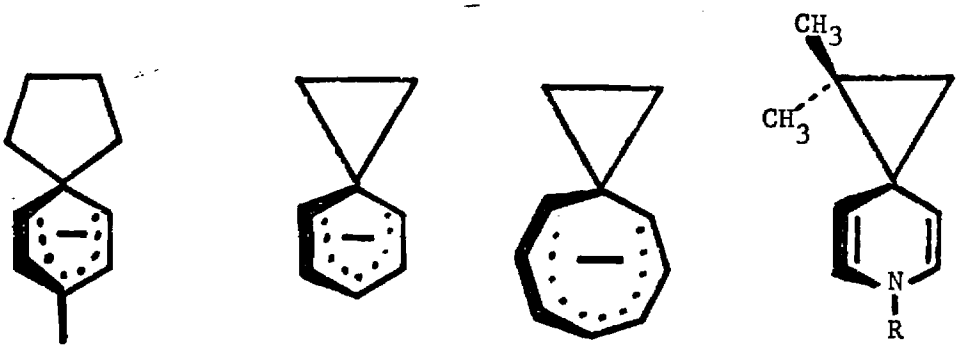
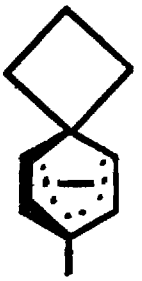
this interpretation is reasonable was indicated by the preparation[2,3] of the stable anion 2 from reaction of 4-chloro-1-p-biphenylylbutane with alkali metals.



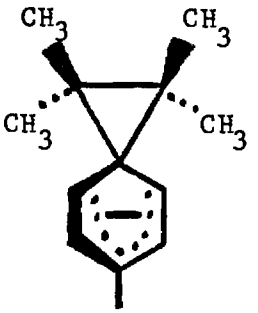
2 3 4 5

Staley and coworkers[4] have reported that attempts to generate the spiro anion 3 by reactions of spiro[2.5]octa-4,7-diene with potassium amide in liquid ammonia at temperatures as low as -65° or with n-butyllithium in tetrahydrofuran-hexane at room temperature resulted only in products in which the cyclopropane ring was opened. In contrast the related species 4 could be prepared[4] in liquid ammonia

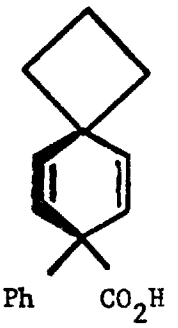
and was stable in this solvent at -30°. This comparative stability is attributable to the fact that the product of cyclopropyl ring opening of 4 would be a non-aromatic cyclooctatetraene derivative whereas that from 3 is aromatic. These observations leave unanswered the question of whether 1 and 3 more nearly represent transition states or reaction intermediates. That various nitrogen analogs 5 of the carbanion 3 have been synthesized[5] lends encouragement that some derivatives of 3 may be stable. We wish to report preparation and characterization by carbonation of the spiro anions 6 and 7.



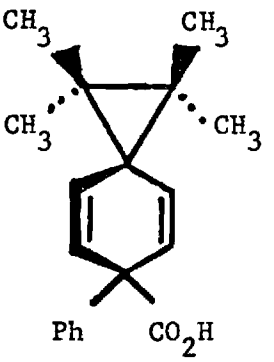
6



7



8



11

Reaction of 2.5 g of 3-chloro-1-p-biphenylylpropane (mp 32-33°)[6a] with 7.7g of Cs-K-Na alloy of eutectic composition[6b] in tetrahydrofuran (THF) at -75°, according to a general procedure already described[2b], gave a red solution which, as soon as it turned green-black, was carbonated (total reaction time of one minute). The usual work-up gave, according to a quantitative GLC analysis 36% yield (based on starting chloride) of 8, 14% of p-biphenylylacetic acid, 3% of 2-p-biphenylyl-butanoic acid, and 6% of 4-p-biphenylylbutanoic acid. The identity of 8, mp 130.5-131.5°, as 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid was established after separation by liquid chromatography on silica gel (elution with mixture of ether, cyclohexane, and benzene) and recrystallization from hexane. The analytical and spectral properties of 8 [^{1}H NMR($CDCl_3$) δ 10.4 (1 H, broad s, CO_2H), 7.31 (5 H broad s), 6.09 (4 H, AB quartet, $\Delta\nu$ = 11.0 Hz, J = 10.2 Hz), 2.08 (6 H, broad s); λ_{max}^{EtOH} 269 nm (ε 1250); mass spectrum, molecular ion m/e 240] agree with expectations[7] for the assigned structure. We conclude

from isolation of 8 that synthesis of the spiro anion 6 has been achieved. Other experiments in which the product from reaction with Cs-K-Na alloy was carbonated at different time intervals showed that 6 dissappeared in THF at -75° with a half-life of about 13 minutes and had a shorter lifetime at higher temperatures.

Since cyclopropyl and cyclobutyl rings have about the same total ring strain[8], success in synthesis of 6 encouraged us to attempt similar synthesis of the lower homolog (p-phenyl derivative of 3) even though previous attempts had been unsuccessful at -65° and a reaction time of about 30 minutes[9]. Reaction of 2-chloro-1-p-biphenylylethane with excess Cs-K-Na alloy in THF at -75° for one minute before carbonation gave less than 1% (if any) of the desired spiro anion even though some 70% of the starting chloride had been consumed.

Maercker et al.[10] have recently succeeded in stabilizing the cyclopropylmethyl form of a 3-butenyl Grignard reagent by introduction of two gem-dimethyl groups (Thorpe-Ingold effect[11]) onto the cyclopropyl ring. Accordingly synthesis of the spiro anion 7 was undertaken. The necessary chloride, 3-chloro-2-p-biphenylyl-2,3-dimethylbutane (9), was synthesized starting with the known[12] 2-p-biphenylyl-2-propanol which was converted to its methyl ether. The ether was cleaved with Na-K in diethyl ether and the anion carbonated to give 2-methyl-2-p-biphenylyl-propanoic acid (mp 170.5-171.8°). The acid was esterified to give the methyl ester (mp 70.5-71.5°) which upon reaction with methylmagnesium iodide gave 3-p-biphenylyl-2,3-dimethyl-2-butanol (mp 60-61°). The latter upon reaction with thionyl chloride in chloroform gave the desired chloride 9, mp 110-111°. The analytical and spectral properties of 9 [^{1}H NMR ($CDCl_3$) δ 7.3-7.7 (9 H, m), 1.56 and 1.58 (12 H, two overlapping s); ^{13}C NMR ($CDCl_3$) in aliphatic region: δ 77.2 (s), 45.8 (s), 29.3 (quartet), 2.52 (quartet)] agreed with the assigned structure. Moreover 9 reacted with lithium in THF at -75° to give after carbonation

3-p-biphenylyl-2,2,3-trimethylbutanoic acid (10), mp 208-209°. In contrast 9 (0.81 g) reacted with Cs-K-Na alloy (6.0 g) in THF at -75° to give a red solution which as soon as it turned green-black was carbonated (50 sec reaction time). The usual work-up gave, according to quantitative GLC analysis of the methyl ester, 7% of 10 and 28% of 11 (yields based upon starting 9) along with considerable non-volatile acid. The mixture of acids was separated by chromatography on silica gel[13] (0.05-0.20 mm, E. Merck A.-G., Darmstadt) with elution by hexane-ether. Acid 11 has mp 182-183° (dec) and analytical and spectral properties [^{1}H NMR ($CDCl_3$) δ 10.6 (1 H, broad s, CO_2H), 7.34 (5 H, broad s), 6.01 (4 H, AB quarter, $\Delta\nu$ = 20 Hz, J = 11 Hz), 1.19 and 1.14 (12 H, overlapping s): λ_{max}^{EtOH} 269 nm (shoulder, ε 377), 218 nm (ε 21,900); mass spectrum, M^+ m/e 282] in agreement with the structure of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid. The anion 7 which is regarded as a precursor of the acid 11 has a half-life of about 22 minutes under our usual conditions in THF at -75°.

In view of the importance of the structure of anion 7 and the derived carboxylic acid 11 to understanding of [1,2] aryl migrations and because conceivably yet unknown migrations could be occurring to give a carboxylic acid whose properties are merely like those ascribable to 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid, the structure of acid 11 has been determined independently by single-crystal x-ray diffraction analysis.

The acid 11 crystallizes in the triclinic space group $P\bar{1}$ with a = 13.307(6) Å[14], b = 8.349(6) Å, c = 10.217(2) Å, α = 90.75(4)°, β = 126.04(3)°, γ = 104.23(5)°, Z = 2, $d_c = d_m$ = 1.16 g cm^{-3}. The intensity data were measured with a Syntex $P2_1$ four-circle diffractometer, equipped with a graphite monochromator, using the θ-2θ scan technique. The structure, which was solved[15] by direct methods, was refined by least-squares methods (variables

included a scale factor, coordinates of all atoms, and anisotropic thermal parameters for all carbon and oxygen atoms; fixed isotropic thermal parameters of 4.0 were used for all hydrogen atoms) to convergence at R = 0.055 and R_w = 0.059 (256 variables, 2160 observations)[19]. The structure is illustrated in Figure 1.

Fig.1 →

It was thought conceivable that x-ray analysis of 11 would reveal that steric compressions had been relieved on going into 7 from the expected precursor of 7, namely 2-p-biphenylyl-1,1,2-trimethylpropylcesium 12. In fact the C_9-$C_{9'}$ or C_{10}-$C_{10'}$ distance in 11 is 2.490(6) Å or about the same as that calculated (2.51 Å) between gem-dimethyl groups in a hydrocarbon having the usual tetrahedral angle and 1.54 Å C-C bond distance. Also the distance between vicinal (essentially eclipsed) methyl groups in 11, C_9-C_{10} or $C_{9'}$-$C_{10'}$, is 3.016(6) Å or again nearly the same value as that calculated (2.93 Å) similarly for vicinal gauche methyl groups in hexamethylethane. Thus the gem-dimethyl group effect in the present work does not seem to depend upon important relief of steric compression if hydrocarbons can be taken as suitable models for organocesium compounds. Evidently the effect is associated with the destabilizing influence of methyl groups upon the tertiary carbanionic center of 12, an effect which would be expected to accelerate cyclization[20], and the stabilizing influence of methyl groups (especially gem-dimethyl groups) upon cyclopropane rings[21,22].

Acknowledgements. Financial support of this work by the National Science Foundation is gratefully acknowledged. The authors wish to thank Mr. Duncan Cheung for helpful discussions on the solution of structure phases.

Supplementary Material Available: Fractional coordinates (Table I), important bond distances (Table II), important bond angles (Table III), and observed and calculated structure factors (Table IV) (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) H. E. Zimmerman and A. Zweig, J. Amer. Chem. Soc., 83, 1196 (1961); E. Grovenstein, Jr., and L. P. Williams, Jr., ibid, 83, 2537 (1961); E. Grovenstein, Jr., and G. Wentworth, ibid, 89, 2348 (1967).

(2) (a) E. Grovenstein, Jr., S. Akabori, and J.-U. Rhee, J. Am. Chem. Soc., 94, 4734 (1972); (b) E. Grovenstein, Jr., and S. Akabori, ibid, 97, 4620 (1975).

(3) For some related species see G. Fraenkel, C. C. Ho, Y. Liang, and S. Yu, J. Am. Chem. Soc., 94, 4732 (1972); M. Julia and B. Malassiné, Tetrahedron Lett., 2495 (1972).

(4) S. W. Staley, G. M. Cramer, and W. G. Kingsley, J. Am. Chem. Soc., 95, 5052 (1973).

(5) J. J. Eisch and C. A. Kovacs, J. Organometal. Chem., 25, C33 (1970); G. Fraenkel and J. W. Cooper, J. Am. Chem. Soc., 93, 7228 (1971).

(6) (a) All compounds for which melting points are given have analytical and spectral properties which agree with the assigned structures; (b) F. Tepper, J. King, and J. Greer, "The Alkali Metals, An International Symposium Held at Nottingham on 14-22nd July, 1966," The Chemical Society, London, 1967, p 25.

(7) Thus the ^{1}H NMR spectrum of cyclobutane has absorption in CCl_4 at δ 1.96 [K. B. Wiberg and B. J. Nist, J. Am. Chem. Soc., 83, 1226 (1961)].

(8) Cf. J. Hine, "Structural Effects on Equilibria in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1975, p 13.

(9) E. Grovenstein, Jr., and Y.-M. Cheng, J. Am. Chem. Soc., 94, 4971 (1972).

(10) A. Maercker, P. Güthlein, and H. Wittmayr, Angew. Chem. Internat. Edit., 12, 774 (1973).

(11) See G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 460-469

(12) D. T. Mowry, J. Dazzi, M. Renoll, and R. W. Shortridge, J. Am. Chem. Soc., 70, 1916 (1948).

(13) Only about half of acid 11 survived chromatography on this grade of silica gel; on a closely related grade of silica gel the entire acid was converted to an insoluble material which impeded flow through the chromatography column.

(14) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

(15) All computations were carried out on the CDC Cyber 74 System. Standard programs utilized included: Germain, Main, and Woolfson's MULTAN, Zalkin's FORDAP, Iber's NUCLS modification of Busing, Martin and Levy's least-squares program, Busing and Levy's ORFFE, and Johnson's ORTEP. Scattering factors were taken from Cromer and Waber's tabulation[16] for carbon and oxygen; Stewart's hydrogen atom scattering factors[17] were used. Anomalous dispersion factors employed were those given by Cromer[18].

(16) D. T. Cromer and J. T. Waber, Acta Crystallogr., 18, 104 (1965).

(17) R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., 42, 3175 (1965).

(18) D. T. Cromer, Acta Crystallogr., 18, 17 (1965).

(19) $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $R_w = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w(|Fo|)^2]^{\frac{1}{2}}$

(20) Cf the greater rate of addition of tert-butyllithium than of n-butyllithium to ethylene [P. D. Bartlett, S. Friedman, and M. Stiles, J. Am. Chem. Soc., 75, 1771 (1953)]. Also benzylsodium and- potassium add to propylene and isobutylene to produce primary rather than secondary or tertiary carbanions [H. Pines and V. Mark, J. Am. Chem. Soc., 78, 4316 (1956); L. Schaap and H. Pines, ibid., 79, 4967 (1957)].

(21) W. D. Good, J. Chem. Thermodyn., 3, 539 (1971).

(22) The question of whether or not equilibrium may exist between 12 and 7 is being investigated by a deuterium-labeling experiment.

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FIGURE 1. A perspective view of the molecular structure of the acid 11.

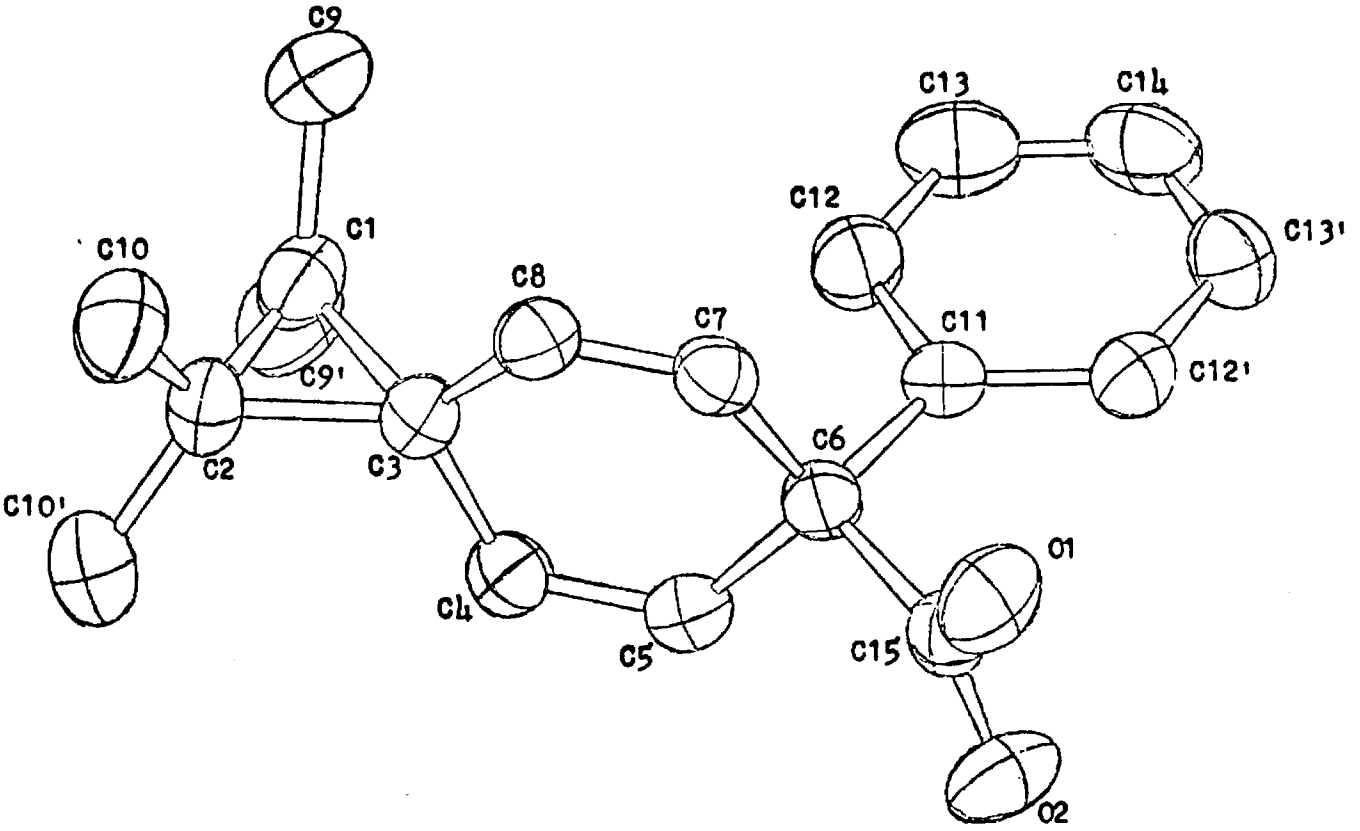

TABLE I. Atomic Coordinates for the Acid 11.

(a) Oxygen and Carbon Atoms

:OM	10^4X/a	10^4Y/b	10^4Z/c
.	3638(2)	3533(3)	3294(2)
!	3901(2)	4275(2)	5580(2)
.	-2600(3)	2738(4)	833(3)
!	-2697(3)	898(4)	826(3)
)	-1217(3)	2268(3)	1669(3)
.	-176(3)	2606(3)	3474(3)
)	1137(3)	2600(3)	4252(3)
)	1722(2)	2185(3)	3378(3)
'	748(3)	2268(3)	1577(3)
)	-563(3)	2304(3)	818(3)
)	-3177(3)	3370(5)	-763(4)
'	-2813(3)	3648(4)	1911(4)
0	-2945(3)	-3(4)	1952(4)
0'	-3318(3)	-289(4)	-724(4)
1	1846(2)	387(3)	3553(3)
2	3123(3)	58(3)	4501(3)
2'	610(3)	-962(3)	2771(4)
3	3141(4)	-1597(4)	4611(4)
3'	646(4)	-2596(4)	2889(4)
4	1916(4)	-2906(4)	3815(4)
5	3188(3)	3426(3)	4136(3)

(b) Hydrogen Atoms

ATOM	10^3X/a	10^3Y/b	10^3Z/c
C4H1	-53(5)	286(5)	412(5)
C5H1	175(5)	278(5)	534(6)
C7H1	104(5)	212(5)	83(5)
C8H1	-112(5)	235(5)	-44(6)
C9H1	315(3)	-275(4)	156(4)
C9H2	422(4)	-317(4)	141(4)
C9H3	275(4)	-450(4)	49(4)
C9'H1	253(3)	-328(4)	-303(4)
C9'H2	374(4)	-356(4)	-133(4)
C9'H3	239(3)	-471(4)	-212(4)
C10H1	398(4)	60(4)	-127(4)
C10H2	253(3)	-58(4)	-301(4)
C10H3	260(3)	90(4)	-215(4)
C10'H1	315(3)	-20(4)	151(4)
C10'H2	298(3)	118(4)	52(4)
C10'H3	430(4)	77(4)	135(4)
C12H1	398(3)	94(4)	504(4)
C12'H1	-26(3)	-76(4)	207(4)
C13H1	401(3)	-185(3)	522(3)
C13'H1	-19(3)	-351(4)	235(4)
C14H1	193(3)	-400(4)	384(3)

TABLE II. Bond Lengths for the Acid 11

Atoms	Distance(Å)	Atoms	Distance(Å)	Atoms	Distance(Å)
C1-C2	1.512	C6-C11	1.544	C13'-C14	1.368
C1-C3	1.569	C6-C15	1.524	C1-C9	1.508
C2-C3	1.553	C7-C8	1.330	C1-C9'	1.512
C3-C4	1.467	C11-C12	1.393	C2-C10	1.521
C3-C8	1.484	C11-C12'	1.391	C2-C10'	1.513
C4-C5	1.324	C12-C13	1.383	C15-01	1.263
C5-C6	1.520	C12'-C13'	1.379	C15-02	1.264
C6-C7	1.507	C13-C14	1.355		

TABLE III. Bond Angles for the Acid 11.

Atoms	Angle (°)	Atoms	Angle (°)
C2-C1-C3	60.51	C5-C6-C7	109.90
C2-C1-C9	120.36	C5-C6-C11	108.08
C2-C1-C9'	121.42	C5-C6-C15	111.38
C3-C1-C9	117.53	C7-C6-C11	110.16
C3-C1-C9'	118.41	C7-C6-C15	108.27
C9-C1-C9'	110.45	C6-C7-C8	123.69
C1-C2-C3	61.56	C3-C8-C7	123.14
C1-C2-C10	119.92	C6-C11-C12	118.23
C1-C2-C10'	119.19	C6-C11-C12'	123.24
C3-C2-C10	118.79	C12-C11-C12'	118.18
C3-C2-C10'	118.32	C11-C12-C13	120.61
C10-C2-C10'	111.13	C11-C12'-C13'	121.17
C1-C3-C2	57.93	C12-C13-C14	121.37
C1-C3-C4	118.35	C11-C6-C15	109.09
C1-C3-C8	116.83	C12'-C13'-C14	119.28
C2-C3-C4	120.57	C13-C14-C13'	119.07
C2-C3-C8	119.77	C6-C15-01	118.37
C4-C3-C8	112.80	C6-C15-02	119.01
C3-C4-C5	123.54	01-C15-02	122.61
C4-C5-C6	123.55		

TABLE IV. Observed and Calculated Structure Amplitudes for Acid 11.

K	L	FO	FC
	H=-14		
0	6	2	2
0	7	1	2
1	6	5	5
1	8	2	2
1	9	5	5
2	6	3	3
2	8	2	2
2	9	1	1
3	4	3	3
3	6	2	2
3	8	1	1
3	9	6	5
4	5	2	2
4	6	6	6
4	7	2	1
4	8	4	4
5	6	2	1
5	7	4	3
	H=-13		
-2	6	3	2
-2	7	6	6
-2	8	3	3
-1	4	1	1
-1	5	4	3
-1	6	5	5
-1	9	5	5
0	5	2	1
0	6	4	4
0	7	6	6
0	8	2	2
0	9	1	1
0	10	4	4
1	3	2	1
1	4	3	3
1	5	5	5
1	7	8	8
1	8	8	8
1	9	5	5
2	3	1	2
2	4	1	2
2	5	3	3
2	8	5	5
2	9	3	3
2	10	2	2
3	5	2	2
3	10	2	2
4	3	2	2
4	4	8	8
4	6	2	2
4	7	1	1
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7	3	1	1
7	4	4	4
7	5	2	2
7	6	2	2
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H= -9

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0	9	3	4
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H= -8

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-4	5	2	2
-4	6	8	8
-4	7	3	3
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K	L	FO	FC
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H= -7

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9	5	2	2

H= -6

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K	L	FO	FC
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-6	8	11	11
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H= -5

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K	L	FO	FC
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5	1	3	4
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7	3	1	1
7	4	4	4
7	6	2	2
8	1	1	2
8	2	2	2
8	3	3	3
8	4	3	3
8	5	1	2
9	2	4	4
9	3	1	2

H= -4

K	L	FO	FC
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-7	5	5	5
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H= -2

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H= 3

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-3	5	2	2
-3	6	2	1
-3	7	3	2
-3	8	2	1
-2	0	10	8
-2	1	9	9
-2	2	23	22
-2	3	4	3
-2	4	1	1
-2	5	10	10
-2	6	4	4
-1	0	22	21
-1	1	2	3
-1	2	10	7
-1	3	15	14
-1	4	5	5
-1	5	6	6
-1	8	3	2
0	0	57	58
0	1	15	15
0	2	2	2
0	3	5	5
0	4	3	3
0	5	4	4
0	6	4	4
1	0	13	13
1	1	2	2
1	3	7	8
1	4	6	6
1	5	5	5
1	6	2	1
1	7	2	2
2	0	28	26
2	1	9	8
2	2	19	19
2	3	2	1
2	6	3	2
2	7	4	3
3	0	8	8
3	1	1	1
3	2	9	8
3	3	3	2
3	4	2	2
4	0	8	7
4	1	4	4
4	2	5	5
4	3	8	8
4	4	8	8
4	5	2	1
5	0	2	2
5	1	8	8
5	2	8	8
5	3	2	2
5	5	1	0
6	0	7	7
6	2	2	2
7	2	1	1

H= 4

K	L	FO	FC
-9	0	4	3
-9	1	1	2
-9	2	3	3
-9	3	5	4
-8	1	5	5
-8	3	1	2
-8	5	5	5
-7	0	7	6
-7	1	1	2
-7	2	4	4
-7	3	1	1
-7	4	5	6
-7	5	3	3
-6	0	1	1
-6	1	7	7
-6	2	3	3
-6	3	23	24
-5	0	18	18
-5	1	8	8
-5	2	2	2
-5	3	14	13
-5	4	17	17
-5	5	1	2
-5	6	1	1
-4	0	2	1
-4	1	5	5
-4	2	7	7
-4	3	10	10
-4	4	8	8
-4	5	4	4
-4	6	2	2
-4	7	3	2
-3	1	13	13
-3	3	4	3
-3	4	14	14
-3	5	4	4
-2	0	8	7
-2	1	18	17
-2	2	3	3
-2	3	17	17
-2	4	2	2
-2	6	2	2
-2	7	1	1
-1	0	13	12
-1	1	13	14
-1	2	5	6
-1	3	2	1
-1	4	3	4
-1	5	6	6
-1	6	3	3
-1	7	2	2
0	0	14	13
0	1	15	16
0	2	2	3
0	3	1	2
0	4	6	7
0	5	11	11
0	6	5	4
0	7	5	4
1	0	31	29
1	1	3	3
1	2	5	6
1	3	4	3
1	5	12	12
2	0	16	14
2	1	7	7
2	2	2	2
2	3	2	3
2	4	10	10
3	0	2	1
3	1	2	2
3	3	17	16
3	4	4	4
3	5	1	1
4	0	2	2
4	1	5	5
4	2	14	14
4	3	5	5
5	1	3	3
5	3	4	3
7	0	1	1

H= 5

K	L	FO	FC
-9	0	5	6
-9	2	2	2
-8	0	4	4
-8	3	6	7
-8	4	1	1
-7	0	7	6
-7	1	3	3
-7	2	3	3
-7	3	3	3
-7	4	6	6
-6	0	8	8
-6	1	13	14
-6	2	14	14
-6	3	3	2
-5	0	13	13
-5	2	13	13
-5	3	7	7
-5	4	5	5
-5	6	3	3
-4	0	15	15
-4	1	1	1
-4	3	10	10
-4	4	4	4
-3	0	8	9
-3	1	8	8
-3	2	3	3
-3	3	11	11
-3	4	4	4
-3	5	4	4
-3	6	1	2
-2	0	11	11
-2	1	3	3
-2	2	3	3
-2	3	11	12
-2	4	13	14
-2	5	3	4
-1	0	44	43
-1	1	2	2
-1	2	7	6
-1	3	5	5
-1	4	10	9
-1	5	4	4
-1	6	5	5
0	0	18	19
0	1	3	2
0	2	6	6
0	3	25	25
0	4	6	6
0	6	6	6
1	0	10	9
1	2	2	2
1	3	23	23
1	4	11	11
1	6	2	1
2	0	1	0
2	1	1	1
2	2	14	15
2	3	7	7
2	4	1	1
2	5	3	2
3	0	1	2
3	1	7	7

K	L	FO	FC
3	2	6	7
3	3	2	2
4	0	3	3
4	1	2	2
4	2	2	2
4	3	7	7
5	0	3	3
5	2	3	2
5	3	4	4
6	0	1	1
6	1	4	4
7	0	1	1
	H=	6	
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-8	1	3	3
-8	2	3	3
-8	3	3	3
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-3	4	8	8
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0	3	15	16
0	4	6	6
0	5	7	7
1	1	12	12
1	2	15	15
1	3	4	4
1	5	1	2
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4	1	6	6
5	0	5	5
6	0	3	3
	H=	7	
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-8	1	5	5
-8	2	2	2
-7	0	5	5
-7	1	5	5
-6	0	11	11
-6	1	9	10
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-5	0	3	2
-5	1	2	2
-5	2	2	3
-5	4	6	6
-4	0	5	5
-4	1	4	5
-4	2	4	4
-4	3	4	4
-4	5	4	4
-3	0	3	3
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-3	2	5	5
-3	3	7	7
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-2	3	4	5
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-1	4	4	4
-1	5	1	1
0	1	8	9
0	2	4	3
0	3	10	10
0	4	6	6
0	5	5	5
1	1	10	10
1	2	5	4
2	0	2	2
2	2	2	2
2	3	5	5
3	2	4	4
3	3	7	6
4	0	1	2
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	H=	8	
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4	1	3	2
	H=	9	
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-3	3	4	4
-2	0	4	4
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-2	3	3	3
-1	0	3	3
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0	2	2	2
1	0	1	2
1	1	2	2
1	2	3	3
2	0	1	1
2	1	1	1
	H=	10	
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-4	2	3	3
-3	0	6	6
-3	2	3	2
-2	0	2	2
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-1	2	2	2
0	0	1	2
0	1	2	2
1	0	1	1
2	0	1	1
	H=	11	
-6	0	7	7
-4	0	2	2
-3	0	2	2

(4-33-610

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

January 26, 1977

TO: Dr. Christopher J. Michejda
Associate Program Director for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

SUBJECT: Annual Report upon
"Chemistry of Carbanions"
NSF Grant No. CHE 76-02720
For Period January 1, 1976-December 31, 1976

During the present grant period the following work has been submitted for publication and copies sent to NSF:

(1) "Carbanions. XVII. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," E. Grovenstein, Jr., and A. B. Cottingham, J. Amer. Chem. Soc. (accepted for publication; should appear shortly).

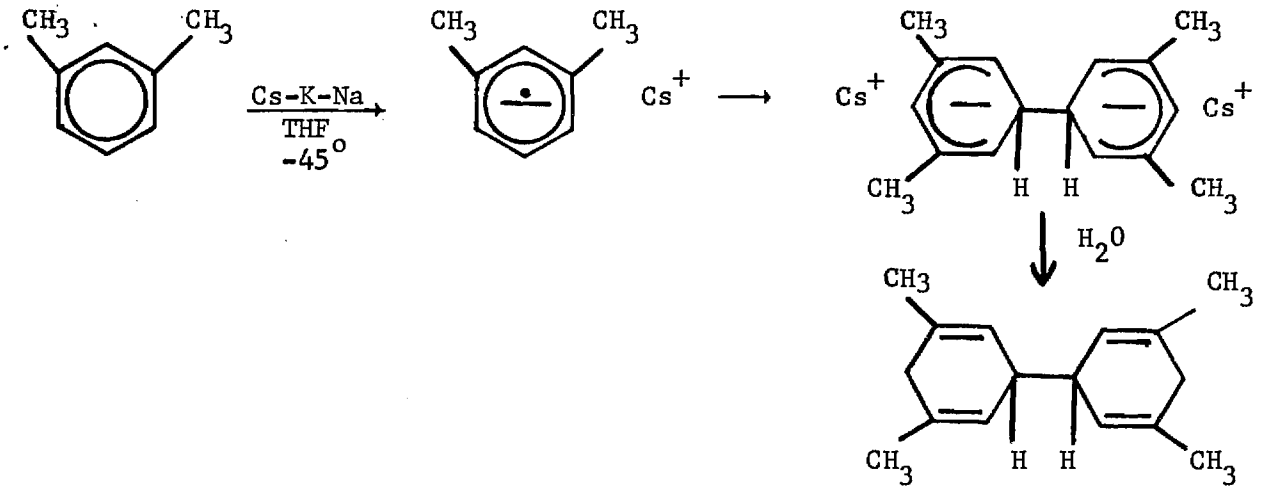
(2) "Carbanions. XVIII. Spiro Anions from Reactions of 2- and 3-p-Biphenylylalkyl Chlorides with Cesium-Potassium-Sodium Alloy," J. A. Bertrand, E. Grovenstein, Jr., P.-C. Lu, and D. Van Derveer, J. Amer. Chem. Soc., 98, 7835 (1976).

(3) "Carbanions. XIX. Reactions of Cesium or Cs-K-Na Alloy with Benzene and Toluene," E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, submitted for publication.

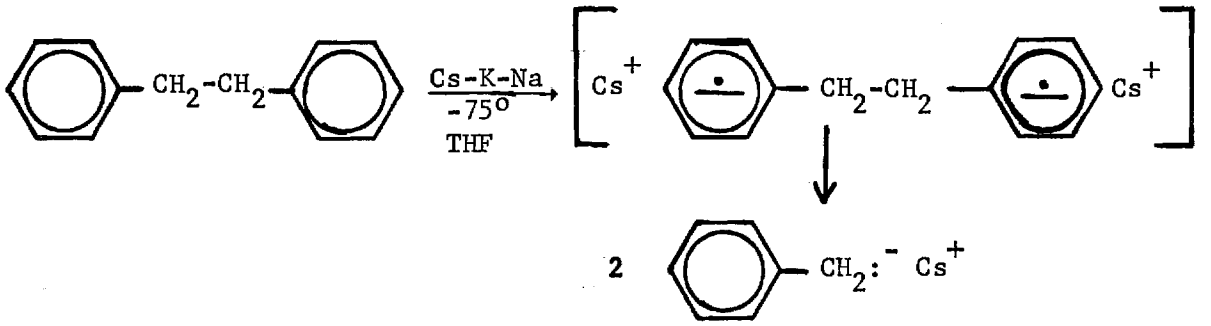
(4) "Aryl Migrations in Organometallic Compounds of the Alkali Metals," E. Grovenstein, Jr., Advances in Organometallic Chemistry, Vol. 16, to appear during coming year.

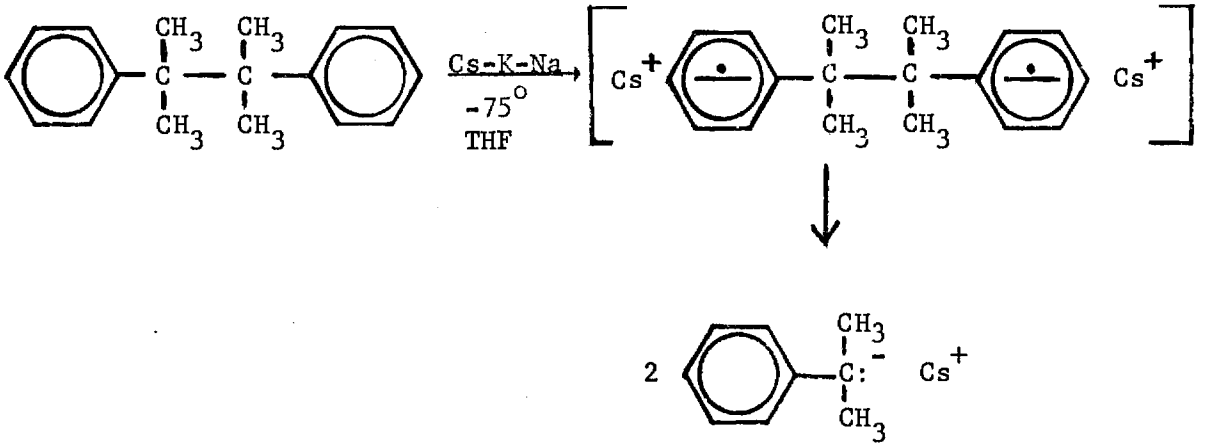
Since a brief technical report has already been sent to NSF for the period of January 1, 1976-August 23, 1976, for purposes of renewal of this continuing grant, this report will concentrate upon more recent developments.

Mr. Dean E. Quest has discovered that in addition to toluene and benzene which form dimers when treated with cesium or Cs-K-Na alloy, that m-xylene forms a similar dimer:

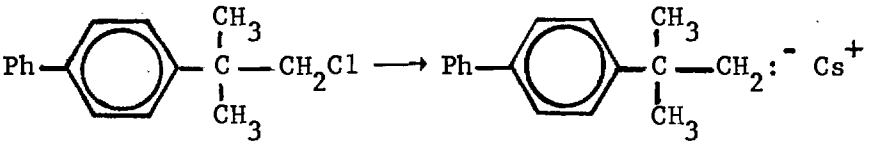


The final product from protonation of the intermediate carbanion is a beautifully crystalline compound which seems to be essentially exclusively the hydrocarbon written above. In contrast, t-butylbenzene and p-xylene fail to yield detectable amounts of dimer upon reaction with Cs-K-Na alloy. Evidently reaction with cesium requires close proximity with the cesium cation; this interaction is blocked by t-butyl and p-dimethyl groups by steric interactions. The cleavage reactions below have been observed to take place readily at the low temperature shown likely by way of intermediate dianions. The yields appear to be quantitative.



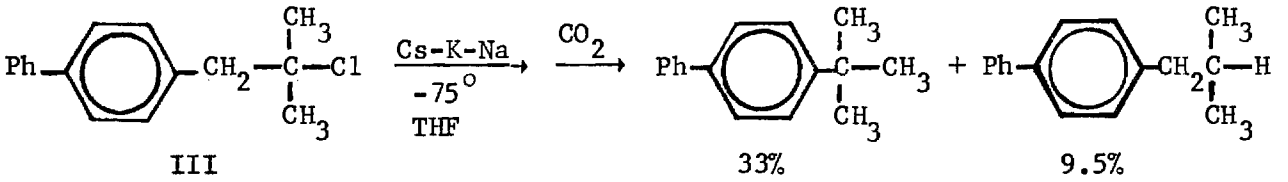


In work of Mr. Pang-chia Lu, whereas the halide I upon reaction with Cs-K-Na

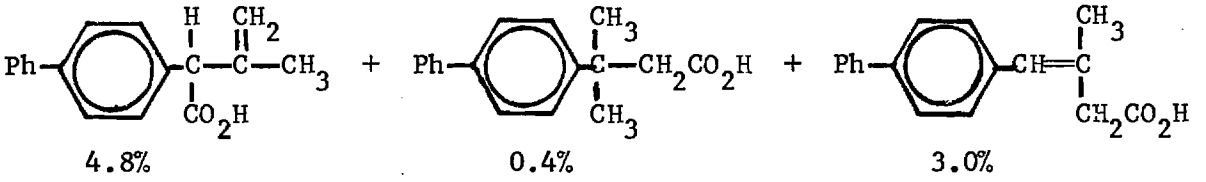


I II

alloy in THF at -75° gave much p-t-butylbiphenyl and products from α-elimination but no products which could be interpreted to come from a 1,2-shift of the p-biphenylyl group in the anion II, the isomeric halide III gave products partially identified as shown below. The considerable quantity of p-t-butylbiphenyl shows

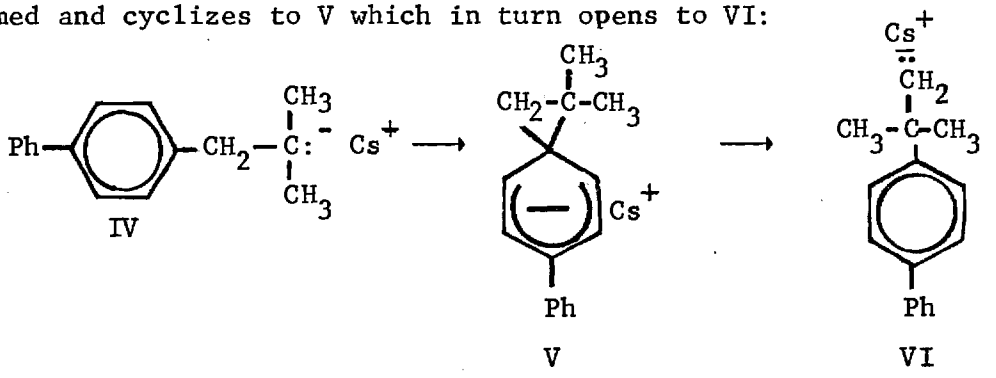


III 33% 9.5%



4.8% 0.4% 3.0%

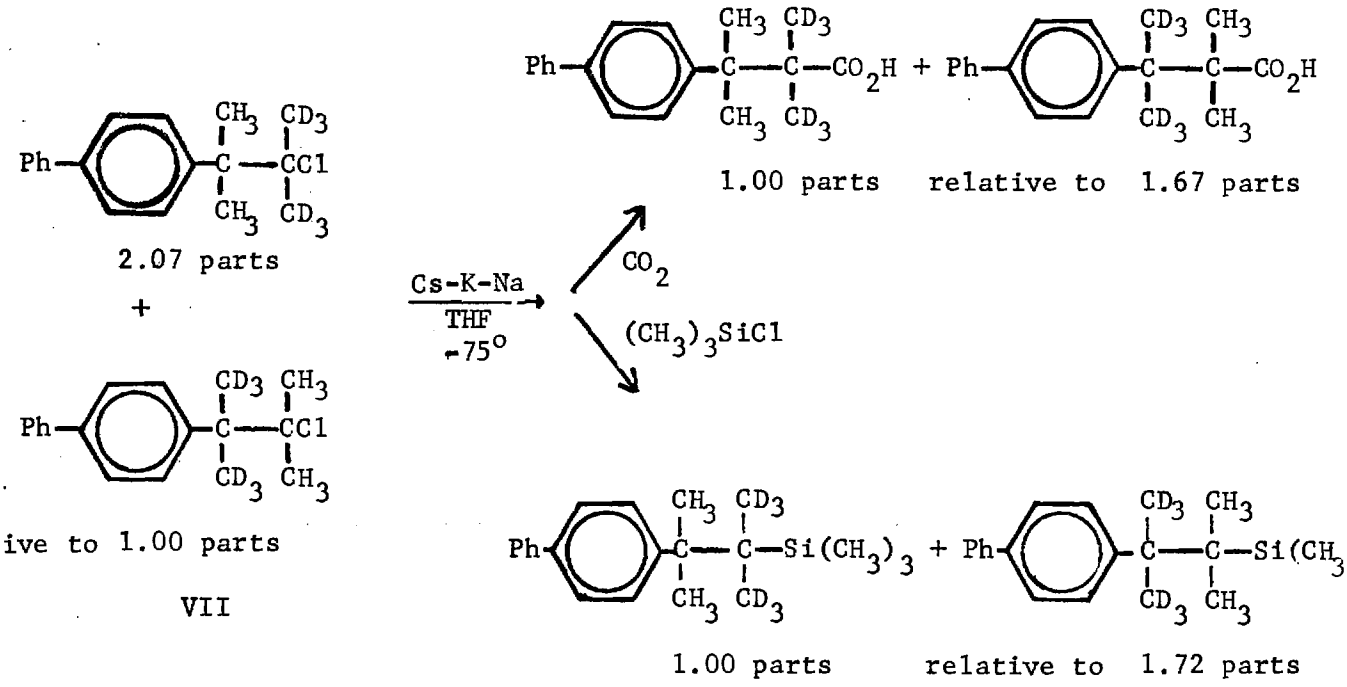
that much p-biphenylyl migration has occurred. Speculatively the anion IV is formed and cyclizes to V which in turn opens to VI:



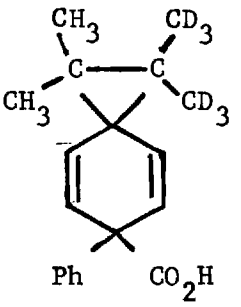
IV V VI

That the spiro anion V opens completely to VI is of interest since the tetramethyl derivative IX (see below) is reasonably stable.

Reaction of the chloride VII, labeled with deuterium, with Cs-K-Na alloy at -75° in THF followed by reaction with carbon dioxide or trimethylsilyl chloride gave the products summarized below:

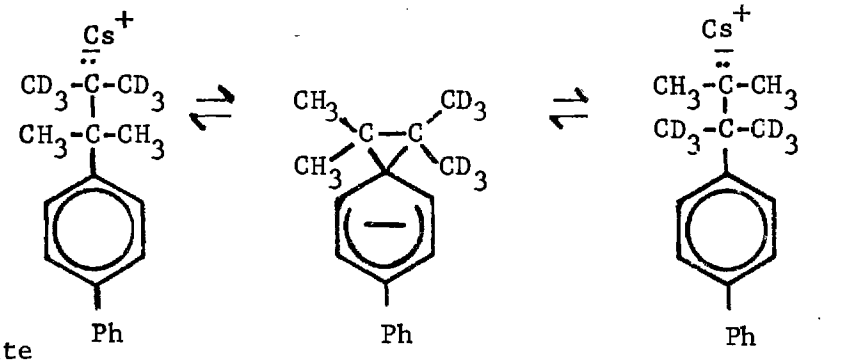


In fact the major acid from carbonation was the spiro acid VIII which was formed



VIII

in some 16 to 20% yield whereas the open chain acid was produced in only 4 to 6% yield. In contrast trimethylsilylation gave 19% yield of the open chain product shown above with little if any (<3%) spirocyclic product. We interpret these results on the basis that the chloride VII reacts with cesium to give the spirocyclic anion IX which is in <u>equilibrium</u> with a lesser quantity of the open anions X and XI.



Approximate Rel. Parts: 1.00 parts 10 parts 1.70 parts

X IX XI

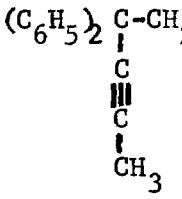
Carbon dioxide appears to react instantaneously with the equilibrium mixture of anions above whereas trimethylsilyl chloride reacts readily but not instantaneously. Hence we judge that carbon dioxide reacts unselectively with IX, X, and XI such that the product ratio of acids corresponds approximately to the equilibrium composition. In contrast trimethylsilyl chloride appears to react considerably faster with the tertiary anions X and XI than with the delocalized anion IX. According to the results of carbonation anion IX has the same half life as X and XI; this result is in agreement with the conclusion that IX, X, and XI are in ready equilibrium.

The results of the deuterium tracer study above show that not only does a rearrangement occur in reaction of chloride VII to give the open chain anions X and XI (doubtlessly rearrangement, i.e., equilibration of deuterium, occurs via the spiro anion IX) but that the products of carbonation and silylation are formed with a large secondary deuterium isotope effect (1.00:1.70). We believe that this isotope effect corresponds to the isotope effect for the equilibrium between X and XI. That this secondary deuterium isotope effect is large has good precedent in the reaction

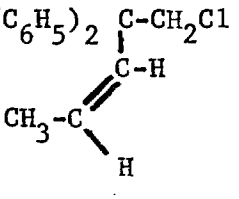
$$(CD_3)_3N: + \overset{\oplus}{H}N(CH_3)_3 \rightleftharpoons (CD_3)_3\overset{\oplus}{N}H + :N(CH_3)_3$$

where ΔG° is reported to be -312 ±30 cal/mole [evidently for the gas phase reaction, see J. F. Wolf, J. L. Delvin, D. J. DeFrees, R. W. Taft, and W. F. Hehre, J. Am. Chem. Soc., 98, 5097 (1976); ΔG° for this reaction in aqueous solution is -255 cal/mole at 0 to 50°C, see D. Northcult and R. E. Robertson, J. Phy. Chem., 73, 1559 (1969)]. If we take ΔG° for the reaction X $\rightleftharpoons$ XI to be two thirds of the gas phase value for the reaction of $(CD_3)_3N$ with $\overset{\oplus}{H}N(CH_3)_3$ because there are two thirds as many CD_3 groups present, then the ratio of XI to X at equilibrium at -75° is indeed calculated to be 1.70 to 1:00 as found.

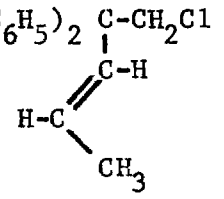
The syntheses of XII, XIII, and XIV are underway by Dr. Kwen-Wai Chui in



XII



XIII



XIV

order to see if 1,2-migration of an acetylene group in XII is competitive with 1,2-migration of phenyl and to study with XIII and XIV the geometry of 1,2-migration of a vinyl group and competition between vinyl and phenyl migration.

Erling Grovenstein, Jr.
Principal Investigator

EG/mw

G-33-610

August 9, 1977

TO: Dr. Kenneth G. Hancock
Program Officer for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

SUBJECT: Brief Technical Report upon
"Chemistry of Carbanions"
NSF Grant No. CHE-7602720
For Period January 1, 1977-August 9, 1977

During the present grant period the following publications appeared on work supported by NSF:

(1) "Carbanions. 17. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds", Erling Grovenstein, Jr., and Auburn B. Cottingham, J. Amer. Chem. Soc., 99, 1881 (1977).

(2) "Carbanions. 19. Reactions of Cesium or Cesium-Potassium-Sodium Alloy with Benzene and Toluene," Erling Grovenstein, Jr., Thomas H. Longfield, and Dean E. Quest, J. Amer. Chem. Soc., 99, 2800 (1977).

The following articles have been accepted for publication:

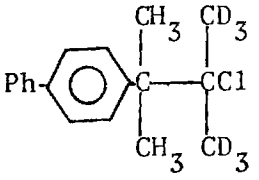
(3) "Aryl Migrations in Organometallic Compounds of the Alkali Metals," Erling Grovenstein, Jr., Advances in Organometallic Chemistry, Vol. 16.

(4) "Skeletal Rearrangements of Organometallic Compounds of the Alkali Metals," Erling Grovenstein, Jr., Angewandte Chemie.

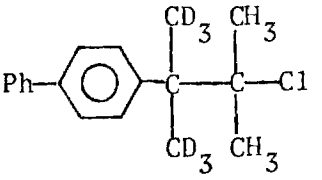
Reprints or copies of manuscripts of these articles have already been sent to NSF.

The Ph.D. thesis of Mr. Pang-Chia Lu on "Spirocyclic Intermediates in the Rearrangements of Organoalkali Compounds" has just been completed. Much of this work was summarized in our Annual Report for 1976. In additional work upon the reaction of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane with alkali metals, the reaction with Cs-K-Na alloy in tetrahydrofuran at -75° has

now been studied with two different ratios of the labeled compounds I and II.

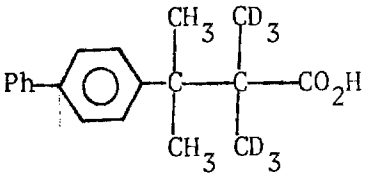


I

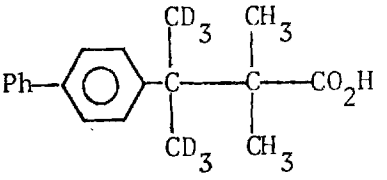


II

Regardless of whether the starting ratio of I to II was 2.0 to 1.0 or 1.2 to 1.0 the ratio of the resultant acids III to IV from carbonation was 1.0 to 1.6.

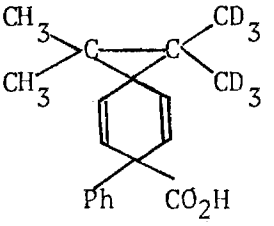


III



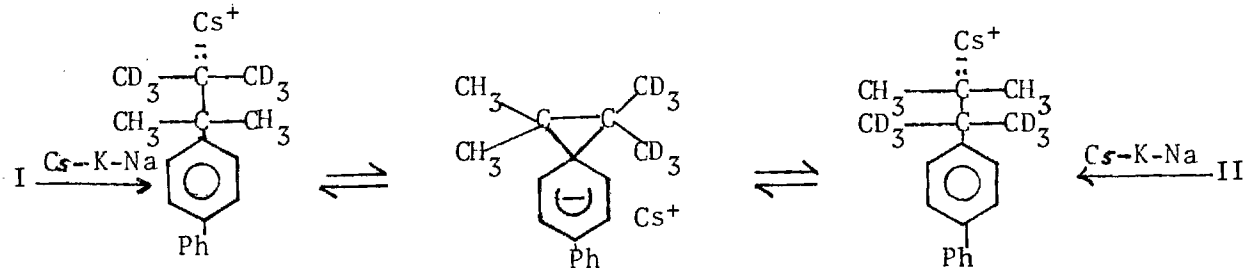
IV

The major product was, however, the spiro acid V. These experimental results



V

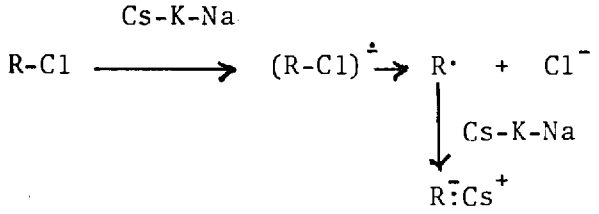
are in agreement with a mobile equilibrium between open and spiro anions VI-VIII.



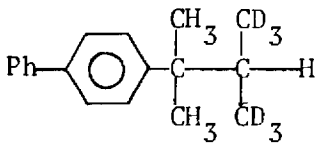
Relative	VI	VII	VIII
Parts:	1.0	9	1.6

While the independence of the ratio of the products III to IV upon the reactant ratio I to II strongly implies that some type of equilibrium is attained, the experiment cited does not make clear whether the equilibrium is attained between the anions VI and VIII or some precursor of these anions. It seems likely that the reaction of alkyl chlorides with alkali metals to

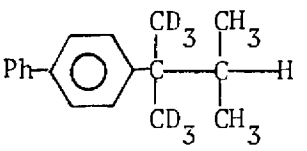
give organoalkali compounds involves the intervention of free radicals as shown below:



Hence the equilibration of the label could have occurred at the stage of an intermediate free radical. That this possibility is unlikely was demonstrate by carrying out the reaction of a 2.0 to 1.0 mixture of I to II in presence of alcohols to serve a proton "traps" for intermediate carbanions. Thus in tetrahydrofuran at -75° in presence of a little tert-butyl alcohol the ratio of IX to X was 1.2 to 1.0; in presence of the more acidic methyl alcohol



IX

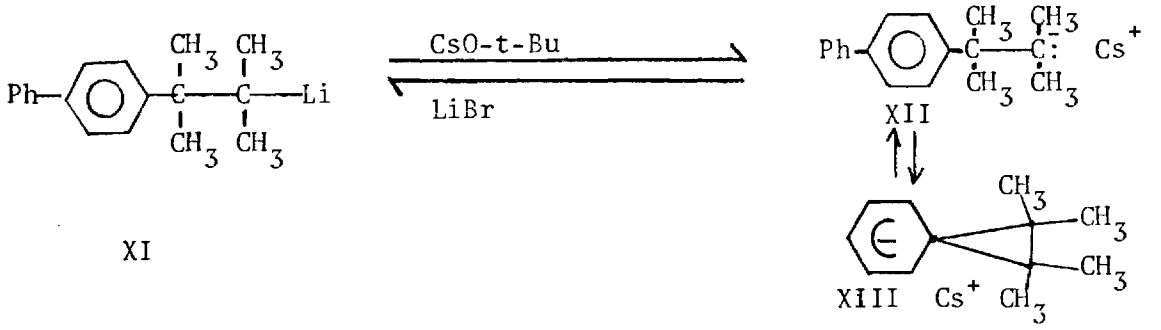


X

the ratio was 1.5 to 1.0 or nearly the same as in the starting chloride. These experiments suggest that the carbanions VI and VIII were formed prior to significant rearrangement; therefore, the rearrangement likely occurs via the spiro anion VII.

Additional evidence in favor of a mobile equilibrium between the anions VI, VII, and VIII comes from experiments with lithium as counter cation. Thus reaction of a 2.0 to 1.0 mixture of the chlorides I to II with lithium metal in tetrahydrofuran at -75° gave an organolithium reagent which upon carbonation contained a 1.0 to 1.6 mixture of III to IV, just as with cesium as counter cation; however, no spiro acid V was produced. Evidently with lithium as cation, while equilibration occurs between the anions of VI, VII, and VIII, yet at equilibrium no appreciable amount of the spiro organolithium compound is present. Evidently, lithium cation prefers to interact with the localized

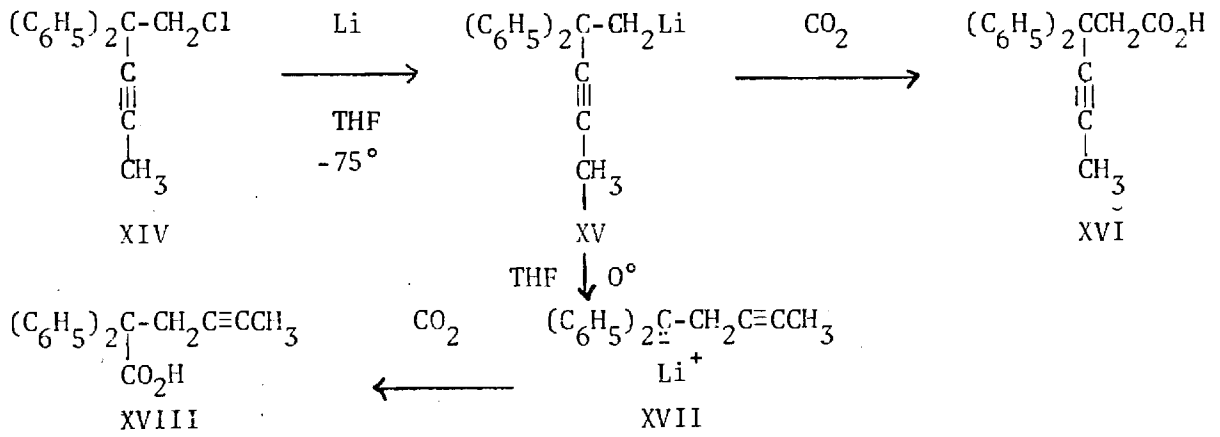
anions VI and VII since such interaction can lead to the usual covalent organolithium compound XI. Furthermore, when the open lithium compound XI



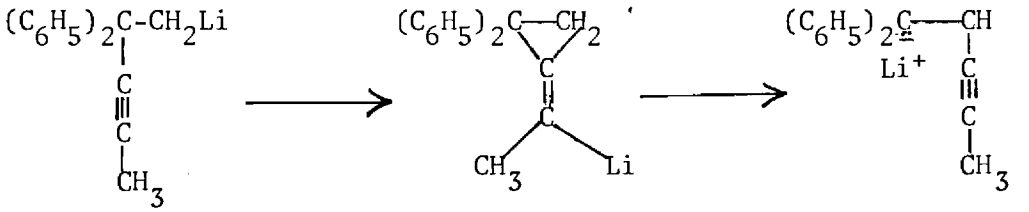
was treated with cesium tert-butoxide at -75° the usual 1 to 2 mixture of open XII to spiro XIII compounds were produced (according to the results of carbonation). Also when the cesium compounds XII and XIII were treated with lithium bromide only the open lithium compound XI was obtained (as deduced from carbonation).

These experiments, along with the earlier experiments summarized in our Annual Report for 1976, convincingly demostrate that spiro anions (cf. XIII) are sometimes stable entities and are formed extremely rapidly from open anions such as XII even at -75°. Hence it is reasonable to presume that spiro anions are intermediates in various [1.2], [1.3], and [1.4] migrations of aryl groups in organometallic compounds of the alkali metals. The Principal Investigator has recently written a summary of all the experimental data available in this field (see Reference 3 cited above).

Dr. Kwen-Wai Chiu has synthesized the chloride XIV and converted it into the corresponding organolithium compound XV by reaction with lithium at

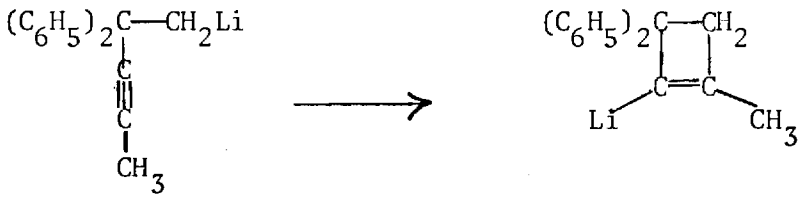


-75°. Carbonation of XV gives the expected acid XVI. When XV is allowed to warm to 0° the rearranged red organolithium compound XVII is produced. The structure of the latter was established by carbonation to give XVIII whose structure was confirmed by independent synthesis as well as by the usual analytical and spectroscopic data. While the mechanism of rearrangement of XV to XVII has not been established, tentatively it is suggested that the migration of the acetylene moiety occurs by way of the intermediate XIX.



XV XIX XVII

This mechanism is analogous to that accepted for migration of vinyl and aryl groups; however, as a 3-Exo-Dig process this ring closure XV → XIX is disfavored by Baldwin's rules. [J. Chem. Soc. Chem. Comm., 734 (1976)]. These rules would favor instead the 4-Endo-Dig process, XV → XX, which, however,

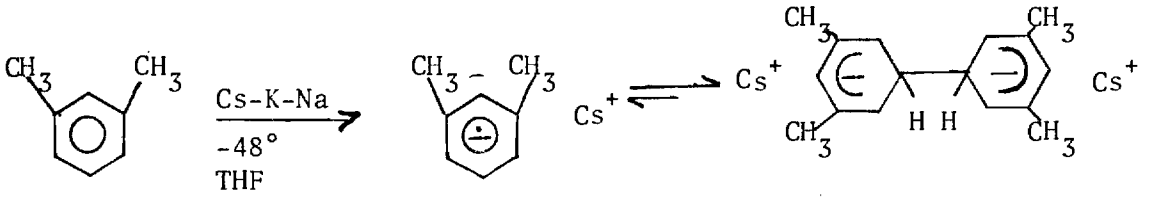


XV XX

would not seem capable of leading to the observed product XVII or XVIII. Experiments are under way to see if XV is converted to XVII by an alternative mechanism, perhaps by an elimination-readdition process.

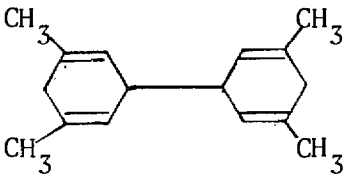
Mr. Dean E. Quest is currently completing his Ph.D thesis on the "Reactions of Cesium Alloys with Aromatic Hydrocarbons and Alkyl Chlorides." Some of his recent work is summarized in our publication, Reference 2, cited above. Whereas m-xylene has been found to react with excess of Cs-K-Na alloy in THF

at -48° to give the corresponding radical anion XXI which largely dimerizes



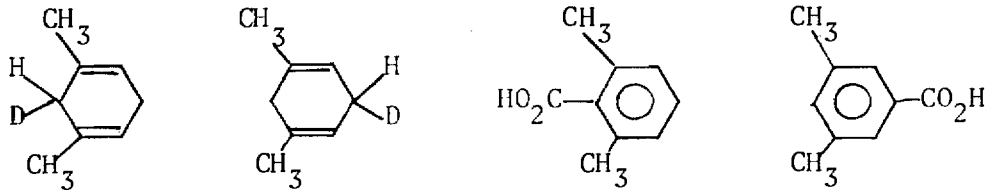
XXI XXII

to XXII (as judged by the yield of the dimeric hydrocarbon XXIII which is ob-



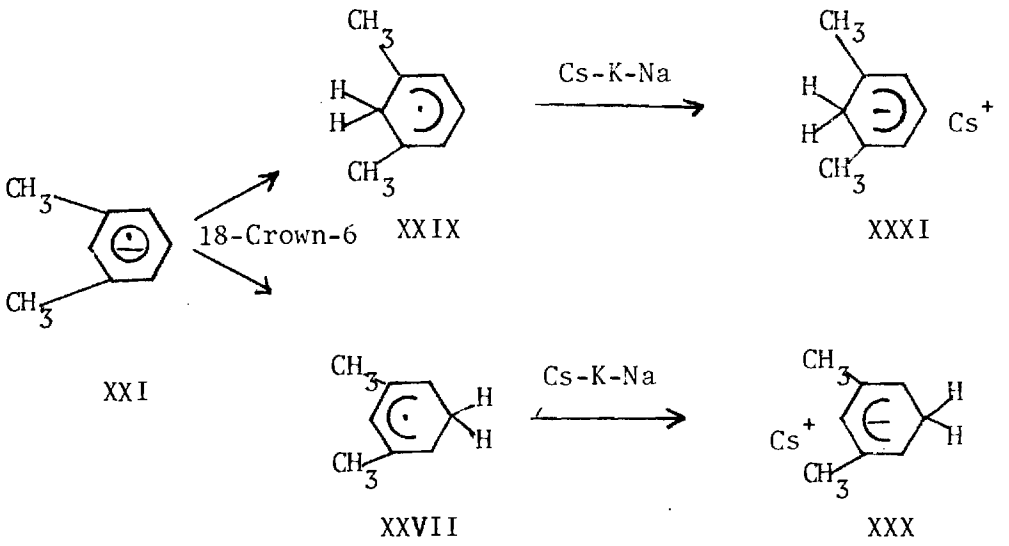
XXIII

tained in some 55% yield upon siphoning the reaction mixture into ice water), reaction of m-xylene with Cs-K-Na alloy in THF in presence of one molar equivalent of 18-Crown-6 gave on protonation after some three hours only monomeric hydrocarbons. For a reaction which was quenched with D_2O, 63.6 mole % of 2,5-dihydro-m-xylene and 33.4 mole % unreacted m-xylene was obtained. According to ^1H and ^{13}C NMR analysis, the 2,5-dihydro-m-xylene was monodeuterated and consisted of a 1 : 3.74 ratio to XXIV to XXV. In another run with two



XXIV XXV XXVI XXVII

molar equivalents of 18-Crown-6 per mole of m-xylene, the acidic product from carbonation and dehydrogenation consisted of about a 1 : 3.86 ratio of XXVI to XXVII. These data are in good agreement with the conclusion that 18-Crown-6 protonates the radical anion XXI to give about a 1 : 3.8 mixture of

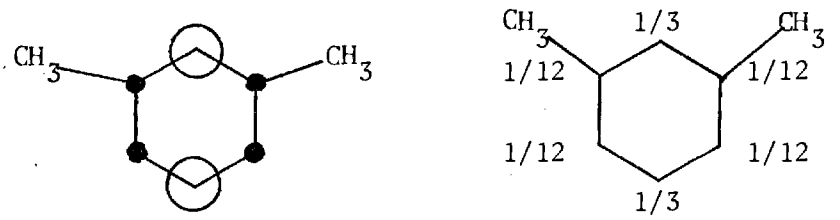


XXI XXIX XXXI

XXVII XXX

radicals XXVIII to XXIX which are reduced to the corresponding ratio of the anions XXX and XXXI.

Note that the chemistry of m-xylene radical anion can be interpreted in terms of the HMO structure XXXI or the charge distribution XXXII (see L.



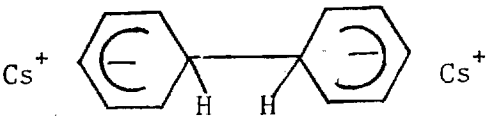
XXXI XXXII

Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin Inc., New York, 1966, p. 255). Dimerization and protonation of the radical anion would be expected to take place at the positions of highest electron-spin density or charge density, hence at positions 2 or 5. Dimerization takes place preferentially at the 5 position since this process leads to the most stable anion XXII when the methyl groups are at the nodal positions in the HOMO (and hence destabilize the anions as little as possible). Protonation, in contrast, occurs preferentially at the 2 position since this process leads to the most stable radical XXIX where the methyl groups are all at centers of high spin density (and hence stabilize the radical as much as possible). The higher regiospecificity in dimerization than in protonation accords with the larger effect of methyl groups in destabilizing anions than in stabilizing

radicals in solution. The theoretical explanation of this substituent effect is still poorly understood but the effect is of considerable importance to free radical and carbanion chemistry.

Reaction of benzene with Cs-K-Na alloy in THF at -43° in presence of two molar equivalents of 18-Crown-6 gave upon carbonation after five hours and dehydrogenation by DDQ 16.8 mole % yield of product (benzoic acid) which largely is derived from the cyclohexadienyl anion XXXIII, 3.6 mole % of products (phthalic and terephthalic acids) which are derived from benzene

XXXIII



XXXIV

radical anion, and 17.6 mole % of product (largely o,o'-, o,p'-, and p,p'-biphenyldicarboxylic acids) derived from the dimer XXXIV of benzene radical anion. Hence somewhat less than half of the benzene radical anion was protonated by 18-Crown-6 in contrast to complete protonation of m-xylene radical anion under milder conditions. These comparative results may be understood on the basis that methyl groups destabilize radical anions and increase their rate of protonation by 18-Crown-6.

G 33610

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

March 13, 1978

TO: Dr. Kenneth G. Hancock
Program Officer for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

SUBJECT: Annual Report upon "Chemistry of Carbanions"
NSF Grant No. CHE 76-02720
For Period January 1, 1977-December 31, 1977

During the present grant period the following publications appeared on work supported by NSF:

(1) "Carbanions. 17. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," Erling Grovenstein, Jr., and Auburn B. Cottingham, J. Amer. Chem. Soc., 99, 1881-1889 (1977).

(2) "Carbanions. 19. Reaction of Cesium or Cesium-Potassium-Sodium Alloy with Benzene and Toluene," Erling Grovenstein, Jr., Thomas H. Longfield, and Dean E. Quest, J. Amer. Chem. Soc., 99, 2800-2802 (1977).

(3) "Aryl Migrations in Organometallic Compounds of the Alkali Metals," Erling Grovenstein, Jr., Advances in Organometallic Chemistry, Vol. 16, pp 167-210 (1977).

The following article has been accepted for publication:

(4) "Skeletal Rearrangements of Organometallic Compounds of the Alkali Metals," Erling Grovenstein, Jr., Angewandte Chemie.

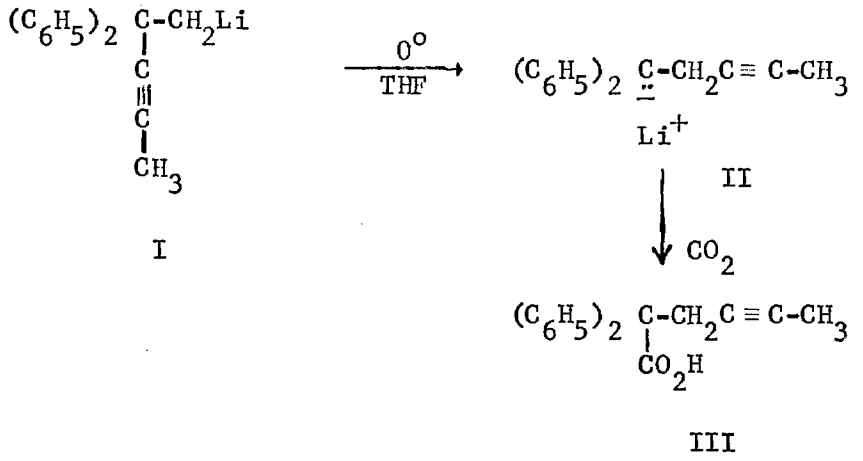
The following article has recently been submitted for publication:

(5) "Phenyl Migration During Preparation of Grignard Reagents," Erling Grovenstein, Jr., Auburn B. Cottingham, and Leslie T. Gelbaum.

Two copies of reprints or manuscripts of these articles have already been sent to NSF.

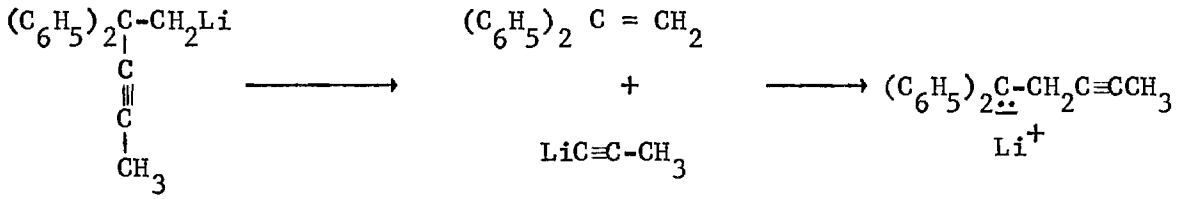
Since a rather detailed report of our work from the period of January 1, 1977-August 9, 1977 has already been sent to NSF for purposes of renewal of this continuing grant, this report will concentrate upon more recent developments.

Dr. Kwen-Wai Chiu has shown that the organolithium compound I is stable in THF at -75° but rearranges at 0° to II whose structure was deduced from the structure

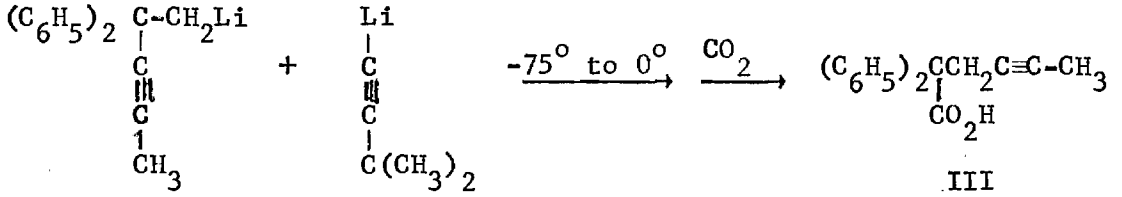


of the carbonation product III. Since this appears to be the first example of migration of an acetylene group in an organolithium compound efforts have been made to establish the mechanism of migration.

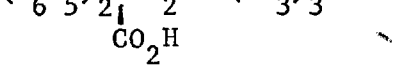
One possible mechanism for rearrangement of organolithium compound I is shown below:



If the above mechanism is valid it should be possible to intercept the intermediate diphenylethylene with another organolithium compound. The test below with the lithium derivative of t-butylacetylene has been carried out.

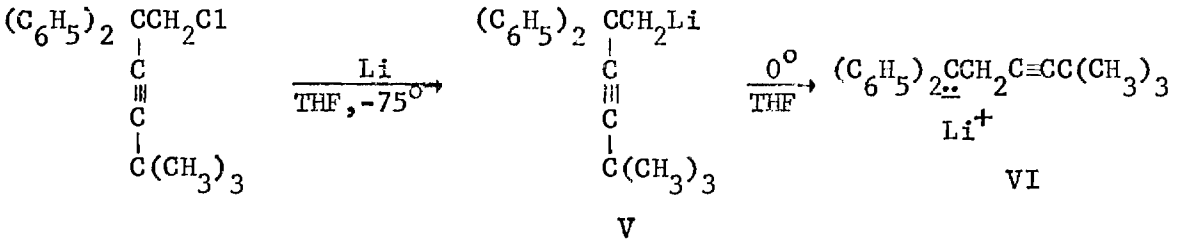


However, only the usual rearrangement product III was obtained and none (< 1%) of the t-butylacetylene incorporation product IV could be detected.



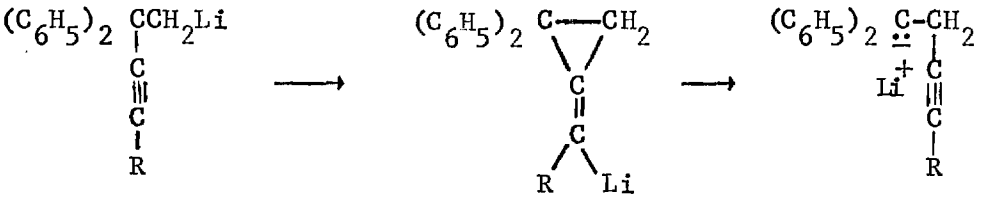
IV

That indeed a t-butylacetylene group is able to undergo a [1,2] sigmatropic rearrangement like the methylacetylene group of I was demonstrated by preparation and rearrangement of V to VI under conditions analogous to those used for rearrangement of I.



V VI

The most likely mechanism for the observed [1,2] migration of acetylene groups in our organolithium compounds is by way of the intermediate VIII.

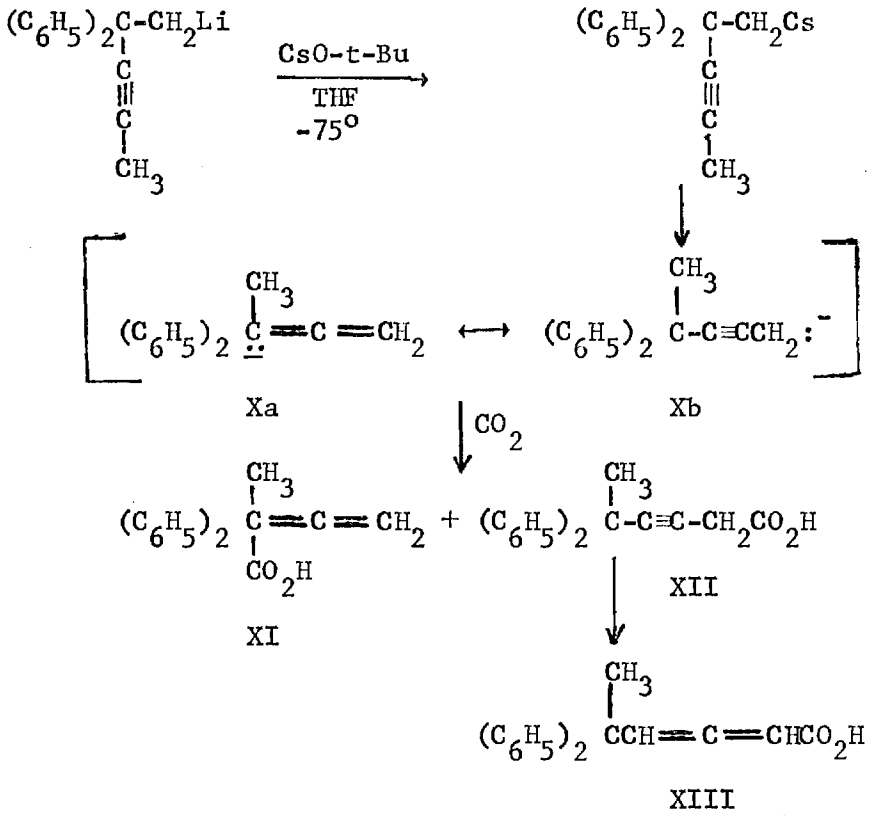


VII VIII

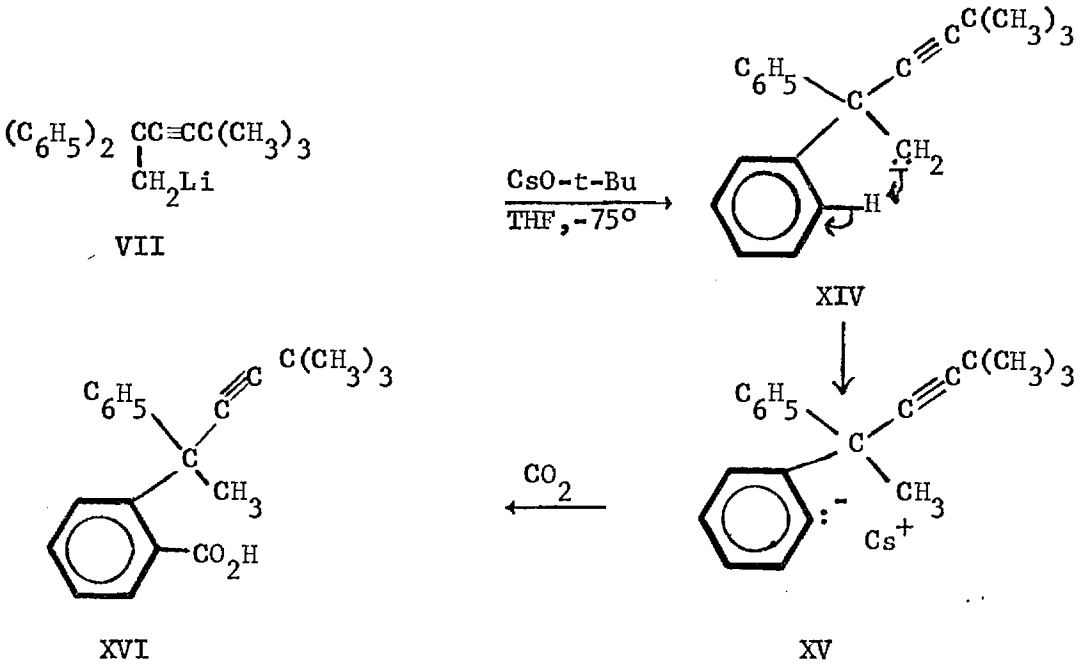
This mechanism is analogous to that accepted for migration of vinyl and aryl groups; however, the ring closure of VII to VIII is an example of a 3-Exo-Dig process which is disfavored by Baldwin's rules [J. Chem. Soc. Chem. Comm., 734 (1976)]. These rules would favor instead the 3-Endo-Dig ring closure of VII to IX which, however, would not appear capable of leading to the observed products II and VI.

VII IX

Since in rearrangements of organoalkali metal compounds the question of which group undergoes migration has been found to be dependent upon the nature of the alkali metal cation (and solvent and temperature), we have attempted to study the rearrangements in the corresponding organocesium compounds. The necessary cesium compounds were prepared by cation exchange with cesium t-butoxide upon the organolithium compound. The results of this experiment proved complex. Evidently the methyl group attached to the acetylene moiety is so acidic that it underwent metallation in the intermediate organocesium compoun to give the mesomeric anion Xa ⟷ Xb which on carbonation afforded XI, XII, and XIII as major products.



In order to avoid such a side reaction the corresponding experiment was next conducted on the t-butyl analog VII. The product of this reaction is tentatively



structure XV since upon carbonation it gives a carboxylic acid whose spectral properties are in agreement with XVI.

Experiments are underway to see if the rearrangement of XIV to XV occurred in a loose or a tight ion pair. If rearrangement occurred in a tight ion pair with cesium as counter cation, [1,2] migration of phenyl would have been expected as in some analogous systems [see E. Grovenstein, Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975)]. Does, therefore the rearrangement of XIV to XV occur in a loose ion pair? If the answer is in the affirmative, then the previous [1,2] migrations of the acetylene moiety evidently take place in a tight ion pair with lithium as counter cation; the lithium cation would, therefore, seem to play an important role in such migrations.

During the current grant period Mr. Pang-Chia Lu and Mr. Dean E. Quest completed their Ph.D. theses on work supported by the present NSF grant. On April 1, Dr. B. Patil will begin work on this grant.

Erling Grovenstein, Jr.
Principal Investigator

EG/mw

G-33-610

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

CHEMISTRY

August 16, 1978

MEMO TO: Dr. Kenneth G. Hancock
Program Officer for Chemical Dynamics
National Science Foundation
Washington, D. C. 20550

FROM: Dr. Erling Grovenstein, Jr.
Principal Investigator
School of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

SUBJECT: Brief Technical Report upon

"Chemistry of Carbanions"
NSF Grant No. CHE-76-02720
For Period January 1, 1978-August 4, 1978

During the present grant period the following publication appeared on work supported by NSF:

"Skeletal Rearrangements of Organometallic Compounds of the Alkali Metals," Erling Grovenstein, Jr., Angewandte Chemie, 90, 317-336 (1978); Angewandte Chemie, International Edition in English, 17, 313-332 (1978).

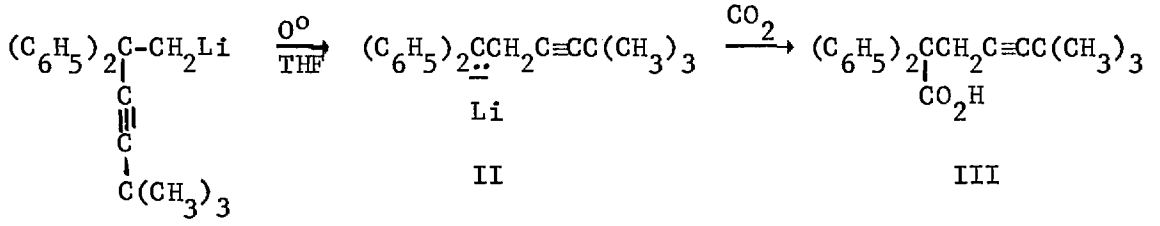
Two copies of the German language edition of this article are enclosed; the English edition will be transmitted as soon as reprints are available.*

The following article should appear in the near future:

* These are now enclosed.

"Phenyl Migration During Preparation of Grignard Reagents," Erling Grovenstein, Jr., Auburn B. Cottingham, and Leslie T. Gelbaum, Journal of Organic Chemistry, 43, (1978).

As mentioned in our Annual Report to NSF for the previous year, Dr. Kwen-Wai Chiu has found that organolithium compound I, while stable at -75°, rearranges at 0° to II whose structure was deduced from the structure of the carbonation product III. Evidence was presented that this

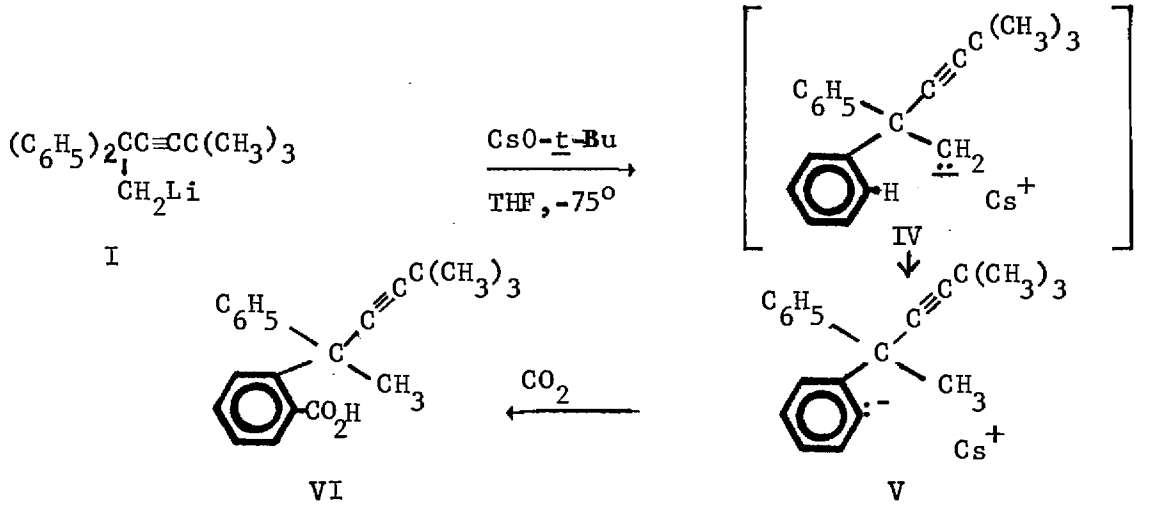


I II III

rearrangement did NOT proceed by elimination of $LiC{\equiv}CC(CH_3)_3$ and readdition of this lithium salt to diphenylethylene to give III. Evidently rearrangement occurs via an intramolecular pathway. To probe the role played by the lithium cation in the above rearrangement, the organolithium compound I was treated with CsO-t-Bu at -75° with the aim of making the corresponding organocesium compound according to the general metathetical process of eq.(1).

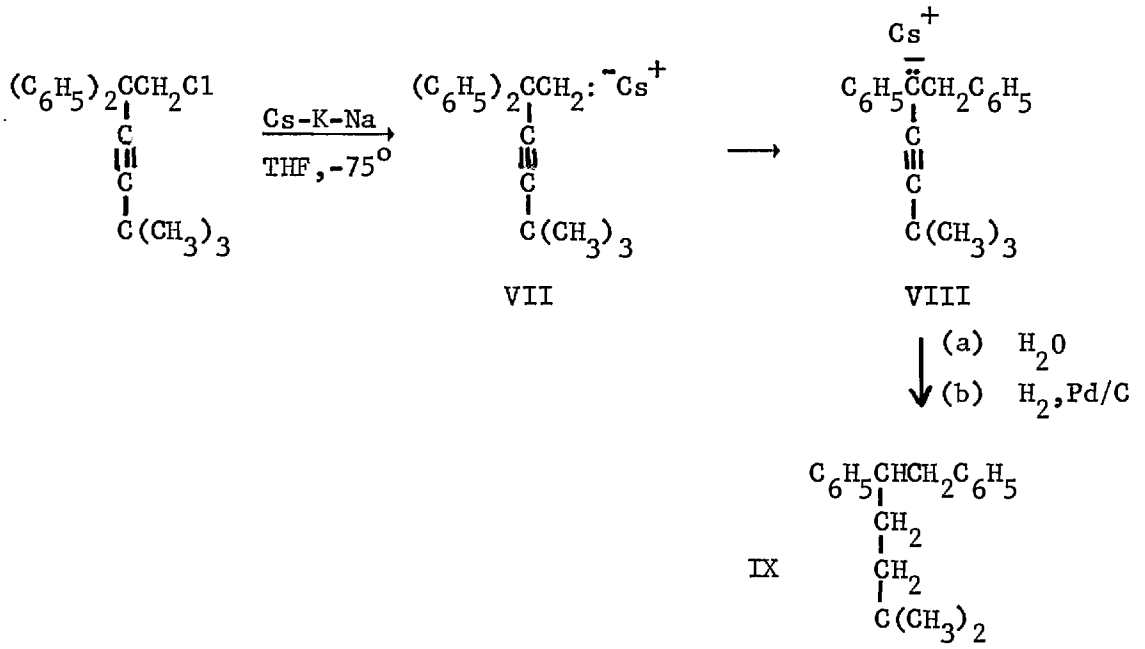
$$RLi + CsO\text{-}t\text{-}Bu \longrightarrow RCs + LiO\text{-}t\text{-}Bu \qquad (1)$$

In fact CsO-t-Bu catalyzed a rearrangement of I even at -75° to the ortho metallation product V.

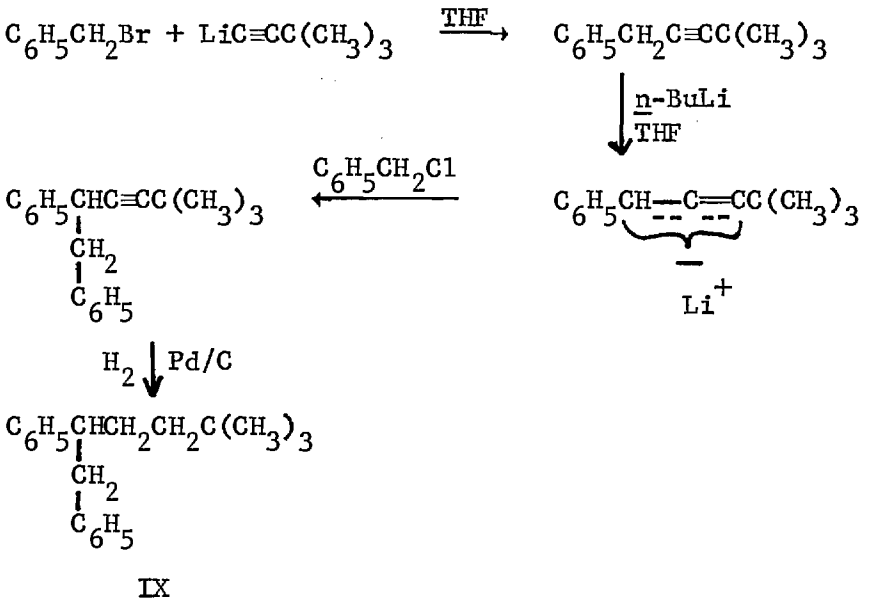


I IV V VI

In new work when the putative organocesium compound was made by reaction of the corresponding chloride with Cs-K-Na alloy in THF at -75° yet another rearrangement product VIII was formed. Compound VIII is the product of 1,2 phenyl migration in the organocesium compound VII. The structure of VIII

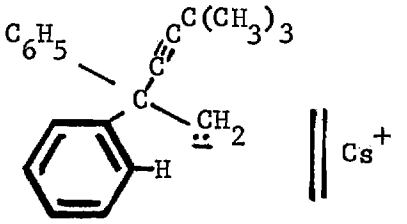


was deduced by protonation and catalytic hydrogenation to IX; for comparison an authentic sample of IX was prepared by the alternative pathway shown below.



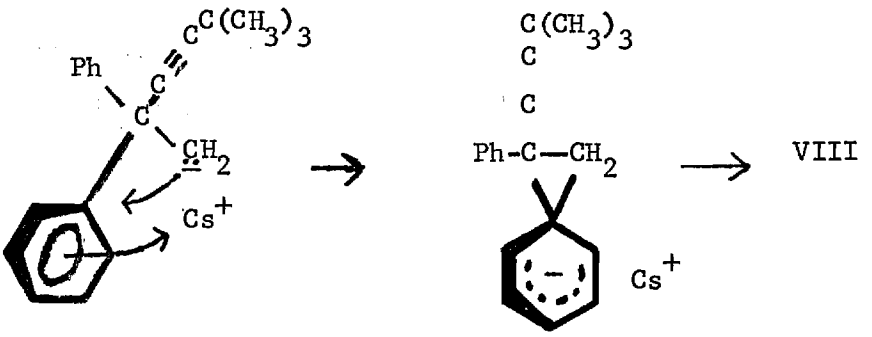
The reaction with Cs-K-Na alloy in addition to yielding IX gave also a tetrahydro derivative, evidently derived from IX by Birch reduction with the excess Cs-K-Na alloy. We are in process of repeating this reaction with the conditions modified to obviate reduction by excess Cs-K-Na alloy.

In summary the above work contains an anamolous result, the expected organocesium compound (IV and VII in the above reaction sequences) yields different products dependent on its method of preparation! Yet IV and VII as formulated above have identical strucutres. We think the answer to this puzzle is that the cesium compound IV formed by the metathesis with CsO-t-Bu is formed as a loose ion pair, IV', which is so reactive



IV'

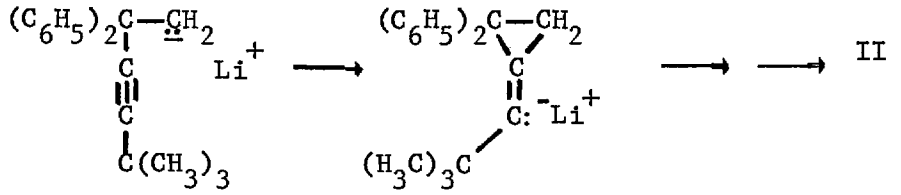
that it removes the first proton with which it comes in contact, this being one of the four ortho protons of the two neighboring phenyl groups. In contrast reaction of the chloride with Cs-K-Na alloy gives VII as a tight ion pair. The cesium cation stabilizes the carbanion both by electrostatic attraction and by blocking access to the carbanion by its large steric size. What such an intimate or tight ion pair does with facility is undergo 1,2 migration of the neighboring phenyl group as shown below. In the transition



X XI

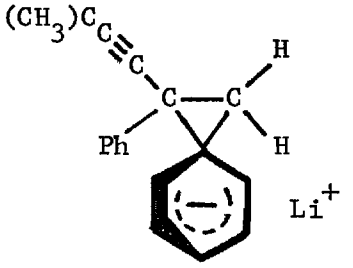
state for this rearrangement the carbon-cesium dipole bends toward the phenyl ring such that the cesium cation remains tightly bound to its counter anion during rearrangement.

If a loose ion pair rearranges to give V, and a tight ion pair (cesium as counter ion) rearranges to VIII, how do we account for the differing rearrangement of the organolithium compound I to the product II with migration of the acetylene group? Our explanation is that the rearrangement of I occurs in a tight ion pair with lithium, XII → XIII as shown below. The



XII XIII

reason why the tight ion pair with lithium (XII) gives migration of the acetylene group whereas the tight ion pair with cesium (X) gives migration of a phenyl group may be dependent upon the fact that lithium cation has an ionic radius (0.60Å) about the size of the covalent radius of carbon (0.77Å) whereas cesium ion has an ionic radius (1.69Å) about the radius of a benzene ring (1.40Å for the ring of carbon nuclei); the net result of electrostatic and other forces of attraction between these alkali metal cations and their gegen anions appears to be that small lithium cations interact better with localized anions as in XII and XIII than with delocalized anions as in XIV whereas large



XIV

cesium cations interact better with the large delocalized anionic system in XI than with the localized anionic charge of X.

Some idea that this conclusion is correct is supplied by simple electrostatic considerations. In order to maximize interionic forces the lithium cation of XIV must be centered as near the center of negative charge as possible, therefore approximately over the center of the 6-membered ring as drawn. While exact dimensions of organolithium compounds in THF solution are unknown, common Li-C distances in crystalline compounds such as ethyllithium[1] and cyclohexyllithium benzene adduct[2] are 2.18 to 2.25Å. These alkyllithium compounds are associated in their crystal lattice; monomeric organolithium compounds, which are likely to be the reactive forms in the present rearrangements likely have a shorter Li-C distance, say 2.04Å. A simple electrostatic calculation shows that in order for the lithium cation to be bound as tightly to the pentadienyl anion system of XIV as to a localized negative charge at 2.04Å, the lithium cation must be 1.48Å above the plane of the pentadienyl anion. Such close approach of a lithium cation to a benzenoid ring system appears unlikely because of severe nuclear repulsions (thus the closest approach[3] of lithium cations to the plane of carbon atoms in crystalline triphenylmethyllithium, benzyllithium, fluorenyllithium, and the dianion of naphthalene is about 2.0 ± 0.1Å).

In contrast a similar calculation for cesium shows that for the cesium cation to be bound as tightly to the pentadienyl system of XI as to a localized negative charge at 3.13Å, the cesium cation must be 2.90Å above the plane of the pentadienyl anion. Such a close approach of cesium appears reasonable in view of the polarizability of large as opposed to small atomic nuclei. Conceivably a still closer appraoch of cesium to the pentadienyl system results in still stronger interaction of cesium with the anion such that the cation-anion interactions in XI exceed that in X. Speculatively covalent interactions (cf bis-π-benzene chromium) may further stabilize XI; Stucky and co-workers[3] have suggested that covalent interactions are important in determining the location of lithium cations above delocalized carbanions. That cesium

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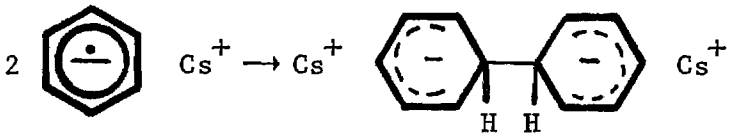
(1) H. Dietrich, Acta Cryst., 16, 681 (1963).

(2) R. Zerger, W. Rhine, and G. Stucky, J. Am. Chem. Soc., 96, 6048 (1974).

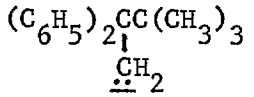
(3) J. J. Brooks, W. Rhine, and G. Stucky, J. Am. Chem. Soc., 94, 7339 and 7347 (1972).

interacts especially strongly with benzene and pentadienyl anions as in XI is confirmed by our recent preparation[4] (on the present grant) of cesium benzenide XV and its dimer (XIV); such compunds are not known with lithium, sodium, or potassium.



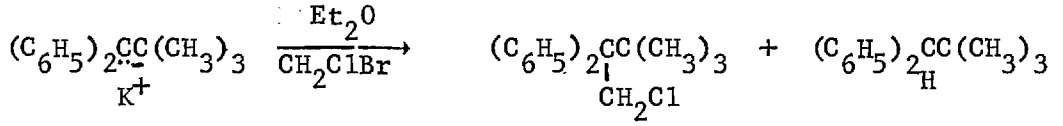
XV XVI

In another area of research Dr. B. B. Patil has begun work on the preparation of the carbanion XVII. This preparation has run into unexpected



XVII

difficulties in that interaction of the precursor XVIII with methylene



XVIII XIX XX

chlorobromide gave only some 17% yield of the chloride XIX and mostly the hydrocarbon XX. Unfortunately the chloride XIX decomposed on attempted purification of the crude reaction mixture by chromatography on silica gel. In another approach the carbanion XVIII has been reacted as shown in the scheme below. Various attempts ($SOCl_2$ + pyridine or CCl_4 + Ph_3P) to convert the alcohol XX to the chloride XIX were unsuccessful (the product were mostly olefins from rearrangement of the corresponding carbonium ion).

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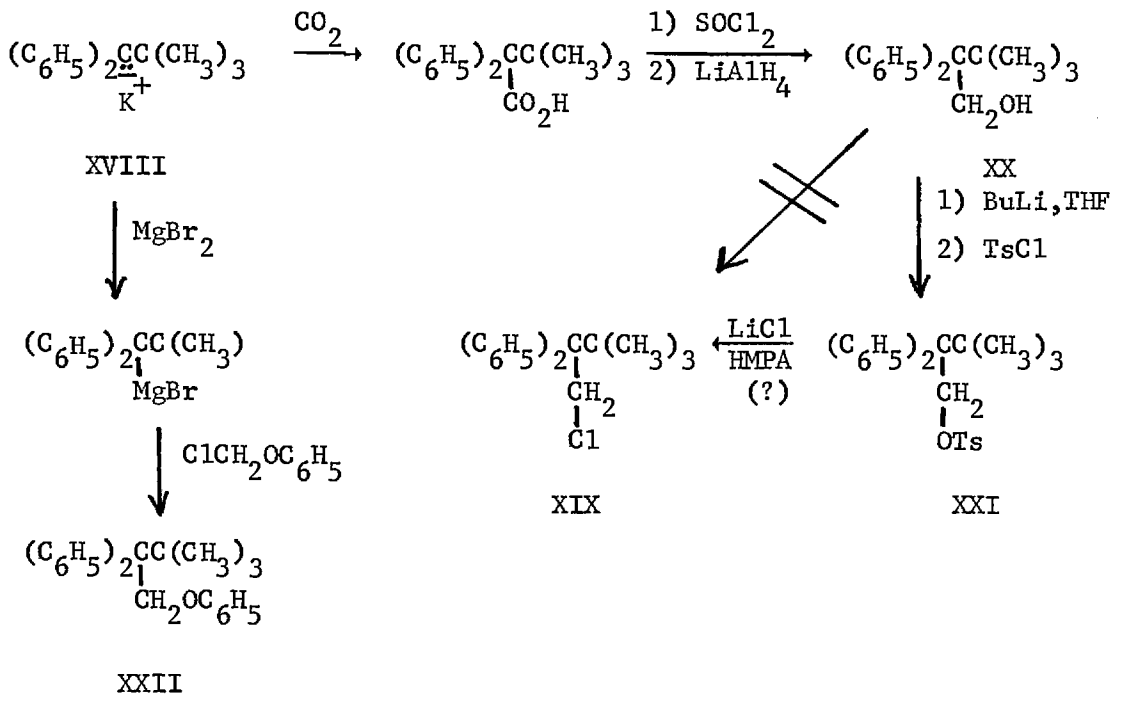
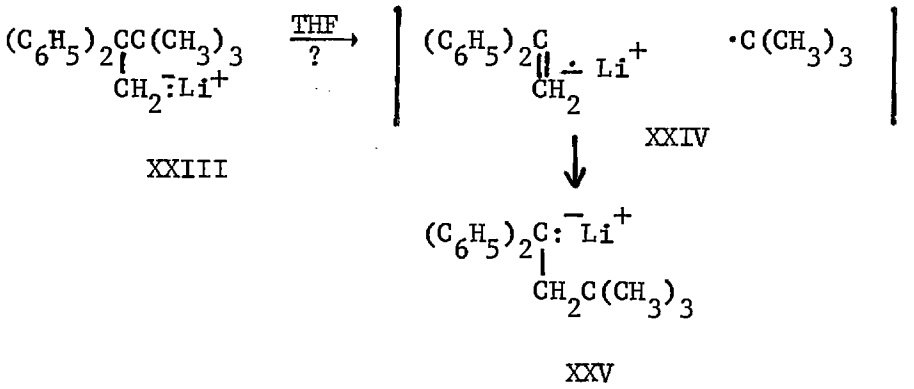
(4) E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).



The tosylate XXI and the phenyl ether XXII have, however, now been successfully prepared. Reactions of these products with alkali metals are planned as sources of the anion XVII. This anion is of interest to see if a 1,2 rearrangement of t-butyl group is observable. Of course, it is the



steric compression in the organolithium compound XXIII and its precursors which has made synthesis so difficult but which likely is needed to promote homolytic cleavage to the radical pair XXIV. The latter likely will collapse to give the rearranged carbanion XXV. While steric acceleration of carbonium ion rearrangements is well known, no corresponding acceleration of carbanion

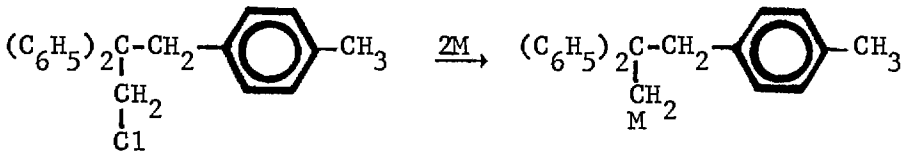
rearrangements has been reported. For purposes of comparison note that cleavage of the hydrocarbon[5] XXVI which has 7.8 kcal/mol of steric strain

$$(CH_3)_3C{-}C(CH_3)_3 \longrightarrow (CH_3)_3C\cdot + \cdot C(CH_3)_3$$

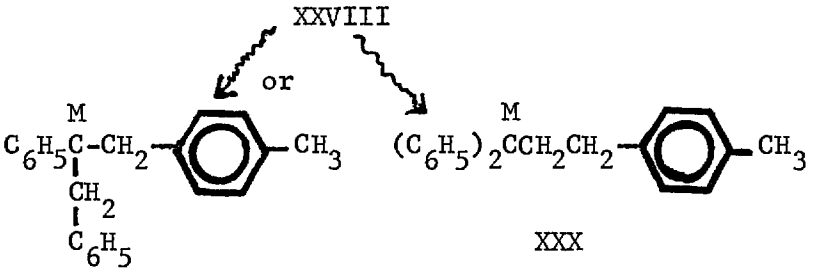
XXVI

is accelerated by a reduction in $\Delta G^{\ddagger}$ of 5 kcal/mole in the transition state.

Finally Mr. Troy Brantley, whose work is only partially supported by the present grant and the remainder by the School of Chemistry, has begun preparation of the chloride XXVII. This chloride will be used to prepare the corresponding organoalkali compounds XXVIII which will be studied for the



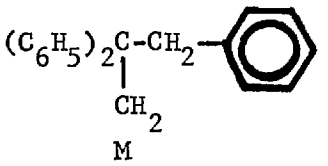
XXVII



XXIX

XXX

ratio of migration of phenyl (to give XXIX) to migration of p-methylbenzyl (to give XXX). The relative rate of these two migrations will be compared to that of the corresponding migrations[6] in XXXI to obtain the substituent



XXXI

(methyl group) effect on the migratory aptitudes. From this data and other information[7] it is believed that the mechanism of 1,2 migration of the benzyl group can be deduced.

Erling Grovenstein, Jr.
Erling Grovenstein, Jr.
Principal Investigator

EG/mw

(5) C. Rüchardt, H.-D. Beckhaus, G. Hellmann, S. Weiner, and R. Winiker, Angew Chem. Int. Ed. Eng., 16, 875 (1977).

(6) E. Grovenstein,Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975).

(7) E. Grovenstein, Jr., and G. Wentworth, J. Am. Chem. Soc., 89, 1852 (1967).

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ATLANTA, GEORGIA 30332

CHEMISTRY

February 7, 1979

Dr. Kenneth G. Hancock
Program Officer
Chemical Dynamics Program
National Science Foundation
Washington, D.C. 20550

Subject: Progress Report upon
"Chemistry of Carbanions"
NSF Grant No. CHE-76-02720
For Period January 1, 1978 - December 31, 1979

Dear Dr. Hancock:

Yesterday the National Science Foundation was mailed a renewal proposal for a new four year period for my current NSF Grant No. CHE-02720. This proposal contains a summary of progress to date upon my current grant. A copy of this progress report is enclosed for your records; pp 8a-14a, Sections B, C, and D give the status of problems under investigation during the current year. Unless you have objections, I would like to consider that this summary of three years of work upon CHE-02720 constitutes the annual report for the grant for the current year

The support which the National Science Foundation gives our work is most substantial and is greatly appreciated.

Sincerely yours,

Erling Grovenstein, Jr.
Brown Professor of Chemistry

EG/jk

Summary of Progress to Date upon "Chemistry of Carbanions"

NSF Grant CHE 76-02720 For Period Jan. 1, 1976 - Dec. 31, 1978

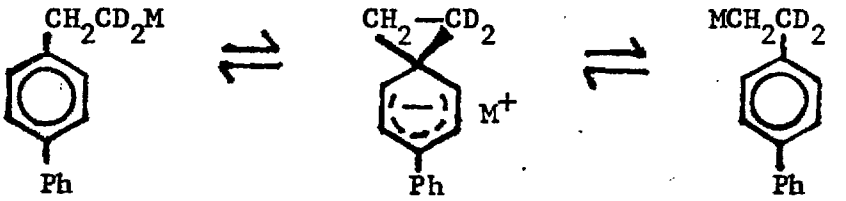
by Erling Grovenstein, Jr., Principal Investigator

PART I. Studies upon Rearrangements of Carbanions

The simplest reaction which a carbanion (i.e., an organoalkali metal compound) can under would appear to be a molecular rearrangement. Since knowledge about the occurrence or non-occurrence of such a reaction would appear necessary for successful procedures using carbani as synthetic reagents and because carbanions are the most useful of the three possible trivalent forms of carbon in organic syntheses, expecially for formation of new carbon-carbo bonds, much of our effort has been directed toward learning the structural features and reaction conditions necessary for rearrangements of carbanions.

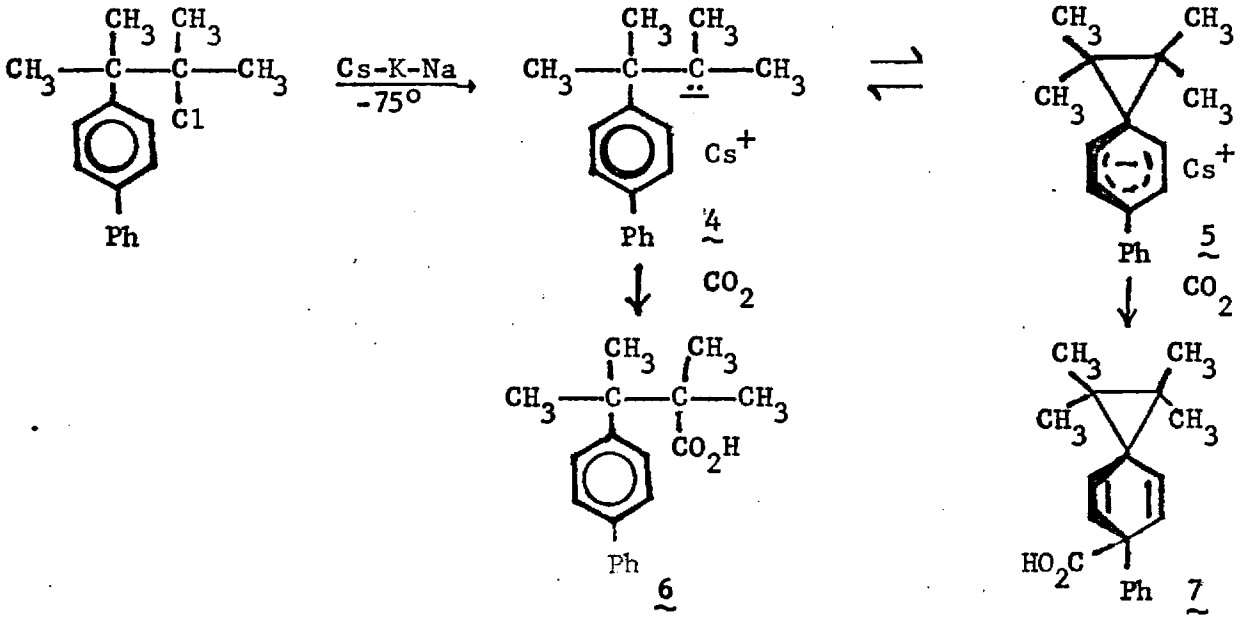
A. [1,2] Migration of p-Biphenylyl in 2-p-Biphenylylethyl Anions and Radicals

Spiro anions have long been suggested as intermediates or transition states in migration of aryl groups in organoalkali compounds. While 2-p-biphenylylethylpotassium and -cesium undergo ready rearrangement[1] (1 → 3) in tetrahydrofuran (THF), attempts to detect the intermediate spiro anion 2 in the reaction of 2-chloro-1-p-biphenylylethane with excess



1 2 3

Cs-K-Na alloy in THF at -75° for one minute before carbonation indicated less than 1% (if an of the desired spiro anion in the reaction mixture even though most of the starting chloride had been consumed. In contrast reaction of 2-p-biphenylyl-3-chloro-2,3-dimethylbutane with Cs-K-Na alloy in THF at -75°C for one minute gave after carbonation some 28% of the spiro acid 7 and 7% of 3-p-biphenylyl-2,3,3,-trimethylbutanoic acid 6 as shown in the scheme below. This work has been published in a preliminary communication[2] which includes

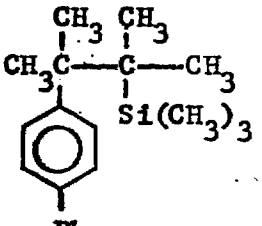


1) E. Grovenstein,Jr., and Y.-M. Cheng, J. Am. Chem. Soc., 94, 4971 (1972).

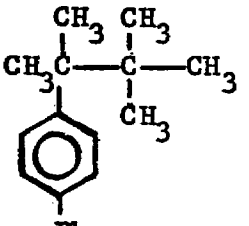
2) J. A. Bertrand, E. Grovenstein, Jr., P. C. Lu, D. Van Derveer, J. Am. Chem. Soc., 98, 7835 (1976).

also an x-ray diffraction study to confirm the structure of 7.

In unpublished work the mobile equilibrium between 4 and 5 has been established by several techniques. First the half-life of the spiro anion 5 and of the open anion 4 are each about 22 minutes in THF at -75°C as determined from the results of carbonation. This finding is surprising for anions of such dissimilar structure as 4 and 5 but can be readily understood if 4 and 5 are in mobile equilibrium. Second the mixture of organocesium compounds 4 and 5 when allowed to react with trimethylsilyl chloride or dimethyl sulfate gives only the open derivatives 8 and 9 respectively and no spiro

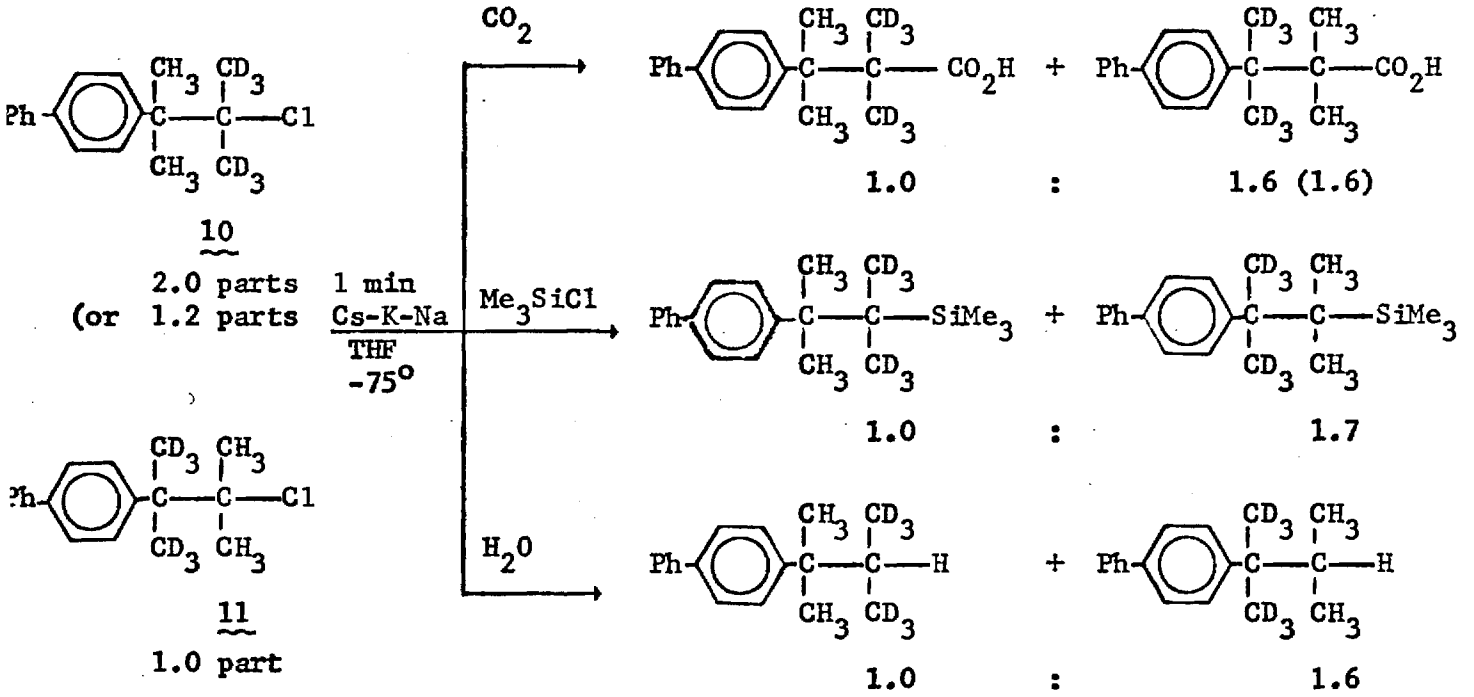


8



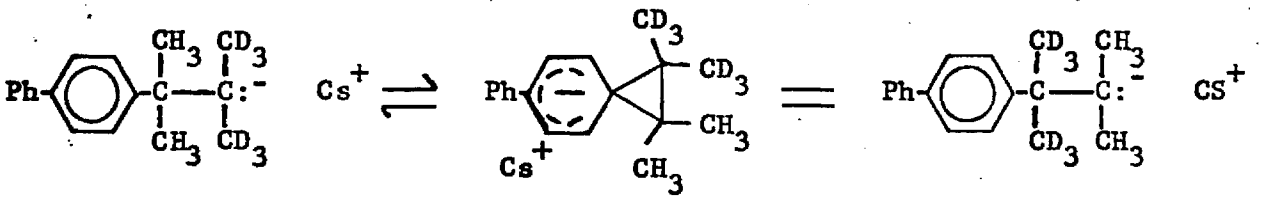
9

products. These results are understandable on the basis that, for a mobile equilibrium (4) ⇌ (5), certain reagents may attack one of the isomeric anions more readily than the other. In particular the less reactive dimethyl sulfate and trimethylsilyl chloride likely react preferentially with the localized anion 4 rather than with the delocalized anion 5 while the more reactive carbon dioxide reacts unselectively with both 4 and 5. Finally confirmation comes from studies with the 2.0 to 1.0 mixture of the deuterium labeled chlorides 10 and 11 respectively which gave the product ratios with various electrophiles as shown in the scheme below:



Note that even when the ratio of 10 to 11 was 1.2 to 1.0 the product ratio on carbonation was identical to that starting with the usual 2.0 to 1.0 ratio of 10 to 11. In summary

the experiments with the deuterium-labeled chloride confirm that cesium alloy reacts with the chloride to give the spiro anion 12 which is in mobile equilibrium with the open anions 13 and 14. If the results of carbonation can be relied upon to measure the position of equilibrium, the equilibrium may be depicted as shown below:

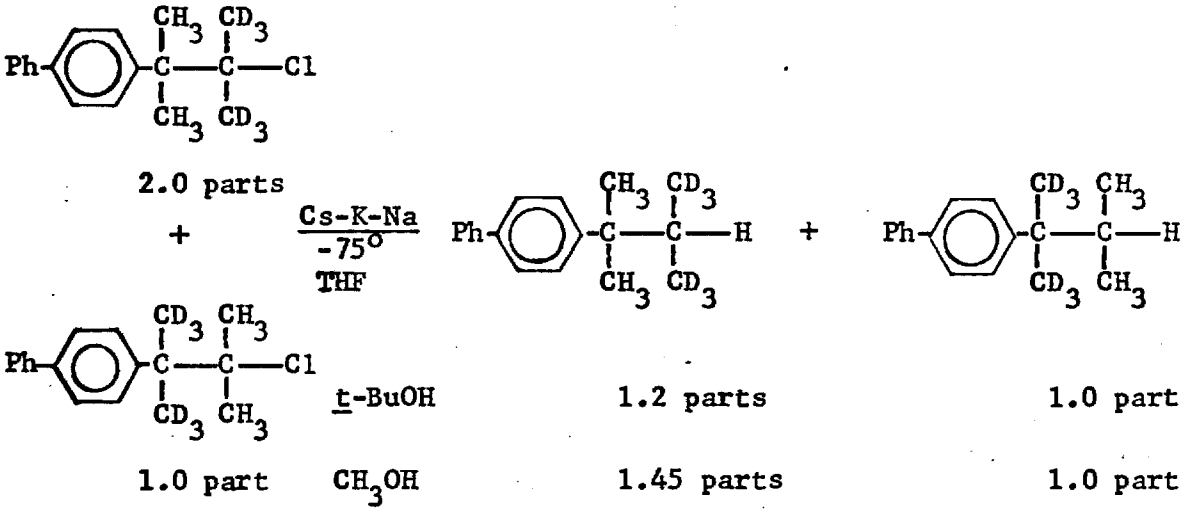


13 12 14

1.0 part 9 parts 1.6 parts

The ratio of 14 : 13 of 1.6 : 1.0 reflects a large secondary deuterium isotope effect and is of the correct magnitude expected for such an effect by analogy to that quoted[3] for $(CD_3)_3N$ in equilibrium with $(CH_3)_3N^+H$ in the gas phase and may be explained in terms of a recent theory[4] of anionic hyperconjugation involving the methyl groups.

The question arises does the rearrangement outlined above in terms of the anions 13 ⇌ 12 ⇌ 14 in fact occur in intermediate free radicals rather than carbanions. We answer this question in the negative on the basis, in part, that it is possible to "trap" the reactive intermediate prior to rearrangement by carrying out the reaction with Cs-K-Na alloy in THF in presence of small amounts of alcohols as shown below. Note that as



2.0 parts

Cs-K-Na, −75°, THF

1.2 parts 1.0 part

1.0 part

t-BuOH

1.45 parts 1.0 part

CH_3OH

the acidity of the alcohol increases from methanol to tert-butyl alcohol the amount of rearrangement decreases. The alcohols should be good "traps" for carbanions but should be less effective in donating hydrogen atoms to free radicals than the solvent tetrahydrofuran[5]. Hence the formation of carbanions from our alkyl chloride precedes the rearrangement step itself.

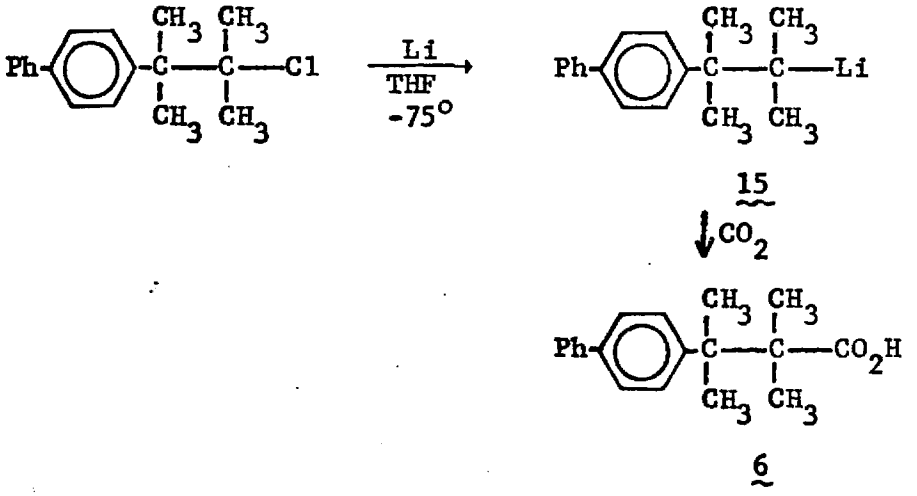
---

[3] J. F. Wolf, J. L. Delvin, P. J. DeFrees, R. W. Taft, and W. F. Hehre, J. Am. Chem. Soc., 98, 5097 (1976).

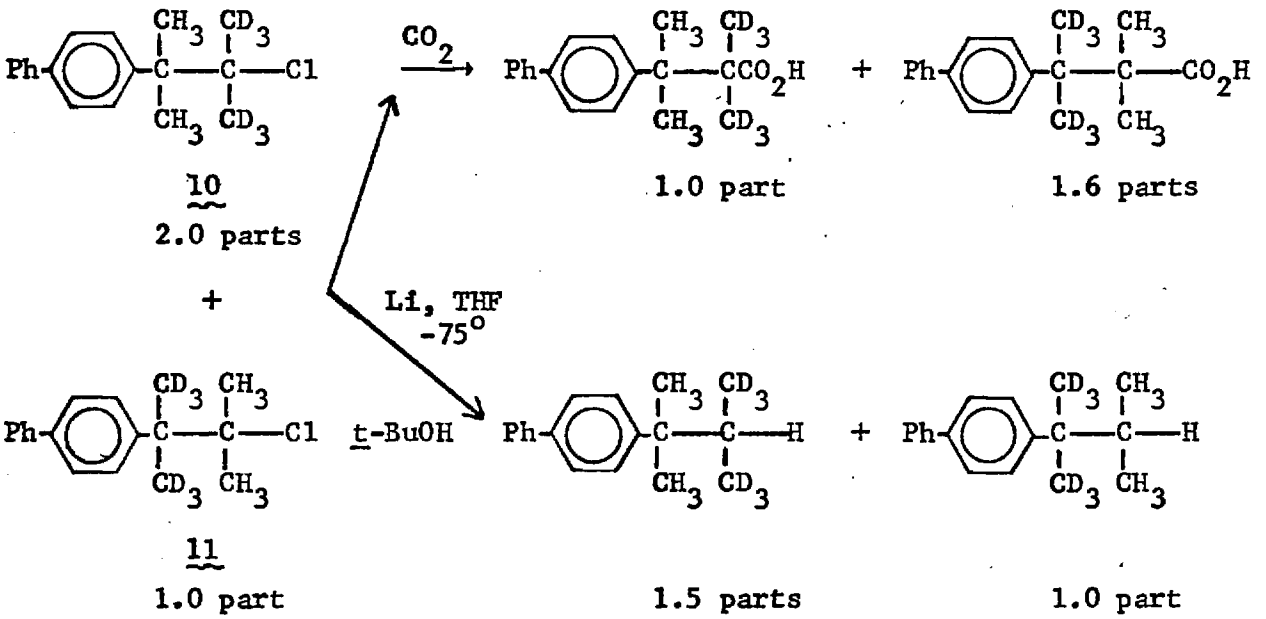
[4] D. J. DeFrees, J. E. Bartmess, J. K. Kim, R. T. McIver, Jr., and W. J. Hehre, J. Am. Chem. Soc., 99, 6451 (1977).

[5] Cf. W. A. Pryor, Chem. and Eng. News, June 7, 34 (1971).

Reaction of 2-p-biphenylyl-3-chloro-2,3-dimethylbutane in THF with lithium metal gives only the open lithium compound 15 with no evidence for appreciable spiro anion as shown by carbonation experiments which give only the acid 6. When, however, the

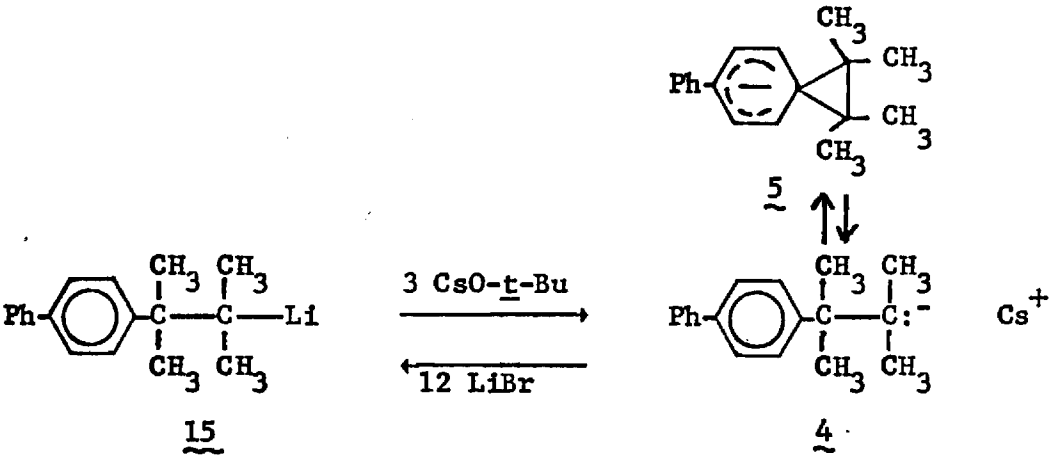


deuterium labeled chloride 10-11 is employed the open acid 6 has the same deuterium distribution as in reaction of the chloride with Cs-K-Na alloy. Obviously the



organolithium compound 15 is undergoing ready [1,2] migration of the p-biphenylyl group. That it is the carbanion (or organolithium compound) which is rearranging rather than a free radical is shown above by "trapping" experiments with tert-butyl alcohol. Again carbanions are "trapped" by the alcohol prior to appreciable rearrangement.

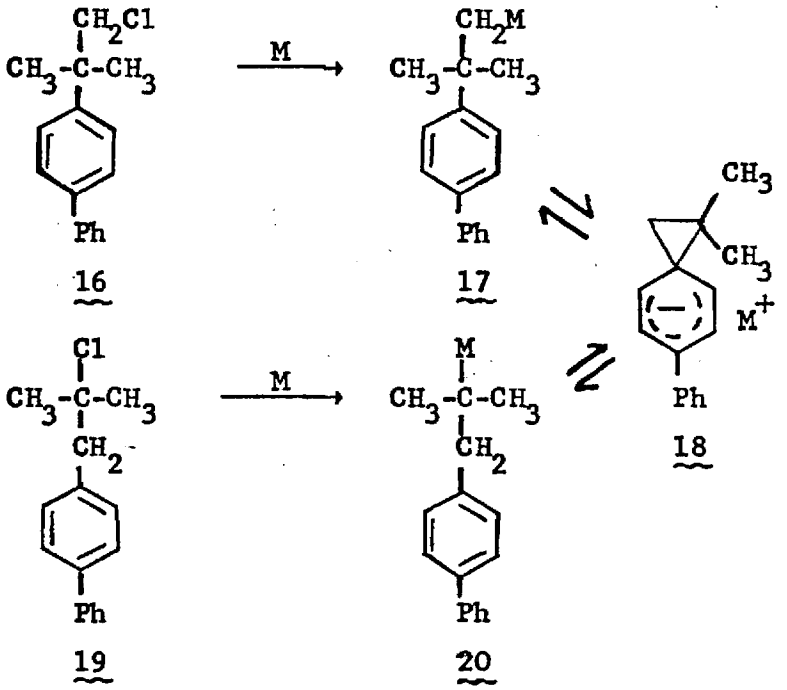
The open organolithium compound 15 serves as a convenient source of the open organocesium compound 4 which is formed by metathesis of 15 with CsO-t-Bu in THF at -75°. Since the open cesium anion 4 is in mobile equilibrium with the spiro anion 5, cesium tert-butoxide serves as a convenient reagent to bring about spiro cyclization at low temperature. Also the equilibrium mixture of 4 and 5 may be converted into the



15 4 5

open organolithium compound 15 by metathesis with LiBr in THF at -75°. These reversible changes (which are established by examination of the products of carbonation), we believe, provide further and convincing evidence that the spirocyclization and [1,2] migration of p-biphenylyl is occurring in a carbanion or organoalkali compound rather than in a free radical.[6] Cation effects similar to those reported here were obtained by Maercker and Roberts[6] in their study of the cyclopropylcarbinyl-homoallyl rearrangement.

Our success in stabilizing the spiro anion 2 relative to the open anion 1 by two pairs of gem-dimethyl groups as in 5 encouraged us to examine the "gem-dimethyl effect" or Thorpe-Ingold effect[7] in greater detail in our carbanionic system. Is one set of gem-dimethyl groups as in 18 adequate to stabilize the spiro anion sufficiently for detection by carbonation techniques? Does [1,2] migration of the p-biphenylyl groups occur in both of the dimethyl derivatives 17 and 20 below? To answer these questions

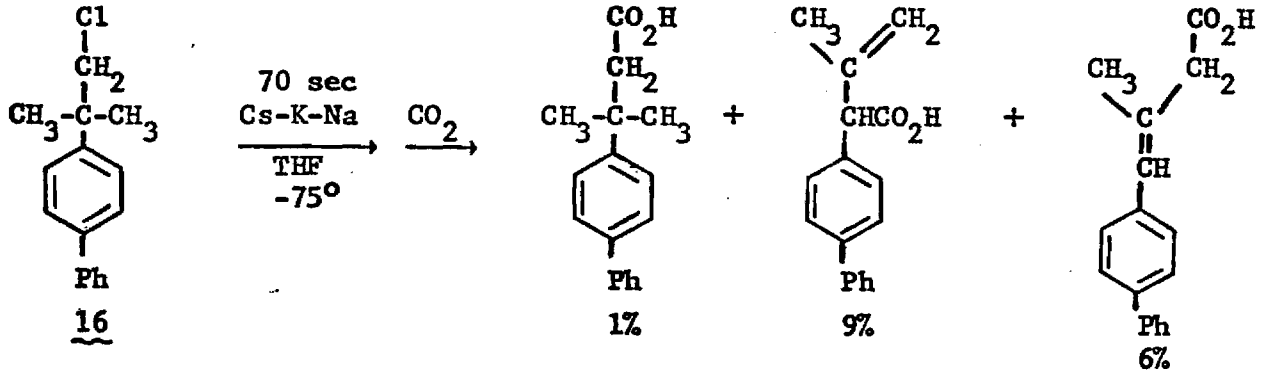


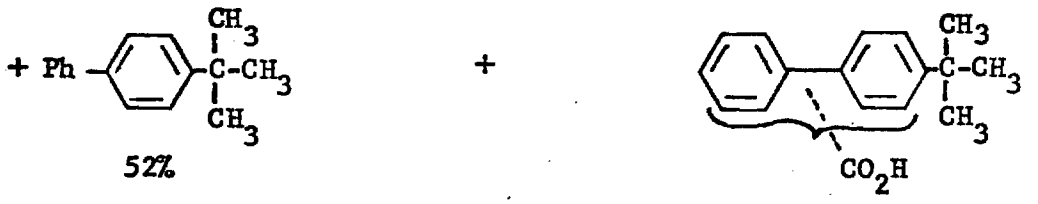
16 17 18 19 20

[6] A. Maercker and J. D. Roberts, J. Am. Chem. Soc., 88, 1742 (1966).

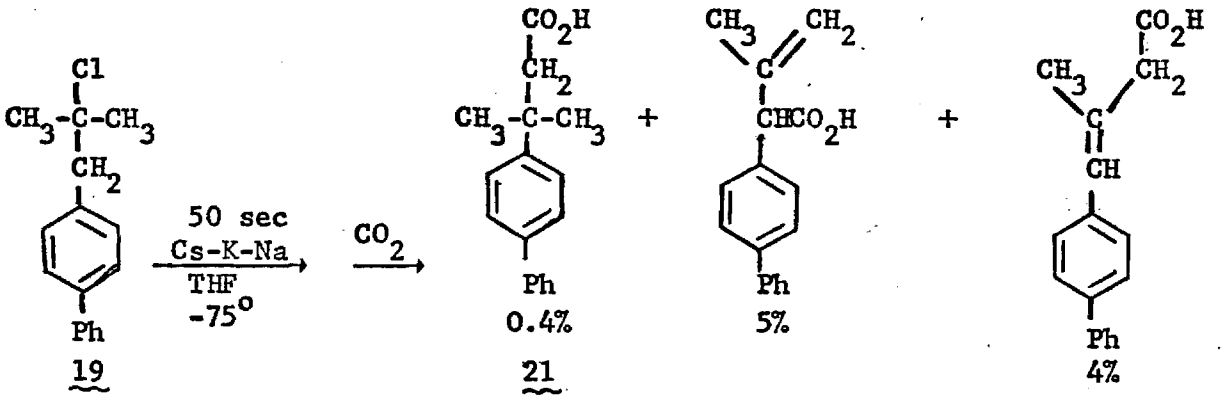
[7] See G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N.Y., 1956. pp 460-469; B. Capon and S. P. McManus, "Neighboring Group Participation," Vol. 1, Plenum Press, New York and London, 1976, pp 58-70.

the two chlorides 16 and 19 were synthesized and allowed to react with Cs-K-Na alloy with the results as summarized in the schemes below.





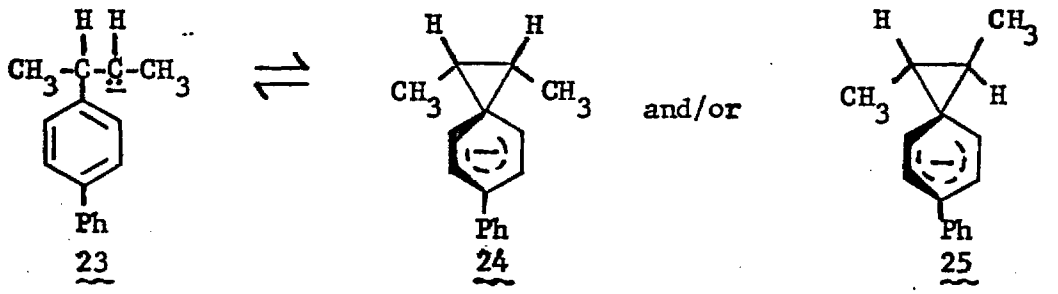
2% of various isomeric acids



22

Neither chloride 16 nor 19 gave any detectable spiro carboxylic acid. While chloride 16 evidently underwent α-elimination with rearrangement of the p-biphenylyl group in a carbenoid intermediate, followed by metallation to give olefinic acids, no evidence for a rearrangement of the type 17 → 18 → 20 was obtained. In contrast chloride 19 gave rise to a small amount of the rearranged acid 21 and an appreciable amount of the rearranged hydrocarbon 22. Evidently the rearrangement 20 → 18 → 17 occurs but not the reverse process. Most of the rearranged product 17 is protonated

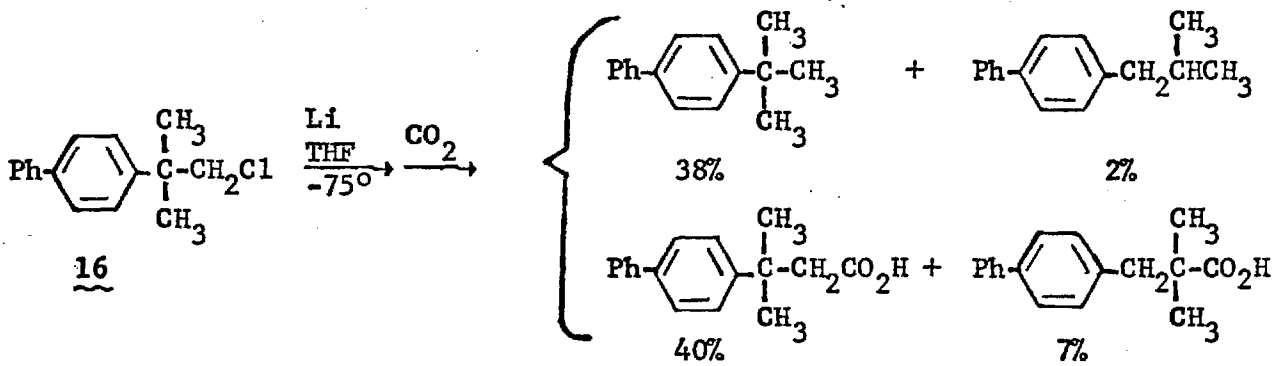
by the solvent (or other acid such as the alkyl chloride) prior to carbonation. We conclude that the gem-dimethyl groups in 20 facilitate rearrangement of the organocesium compound to 17 doubtlessly via the spiro anion 18. Also the primary organocesium compound 17 is thermodynamically more stable than either the tertiary organocesium compound 20 or the spiro anion 18. The destablization of carbanions (organoalkali compounds) by methyl groups is rather well documented[8] for reactions in liquid solution although the theoretical reason(s) for such destabilization is not well agreed upon. Two pairs of gem-dimethyl groups as in 5 appear necessary for stabilization of the spiro anion relative to open forms. It should be emphasized that, at present, it is not known whether two methyl groups situated as in 24 or 25 would be



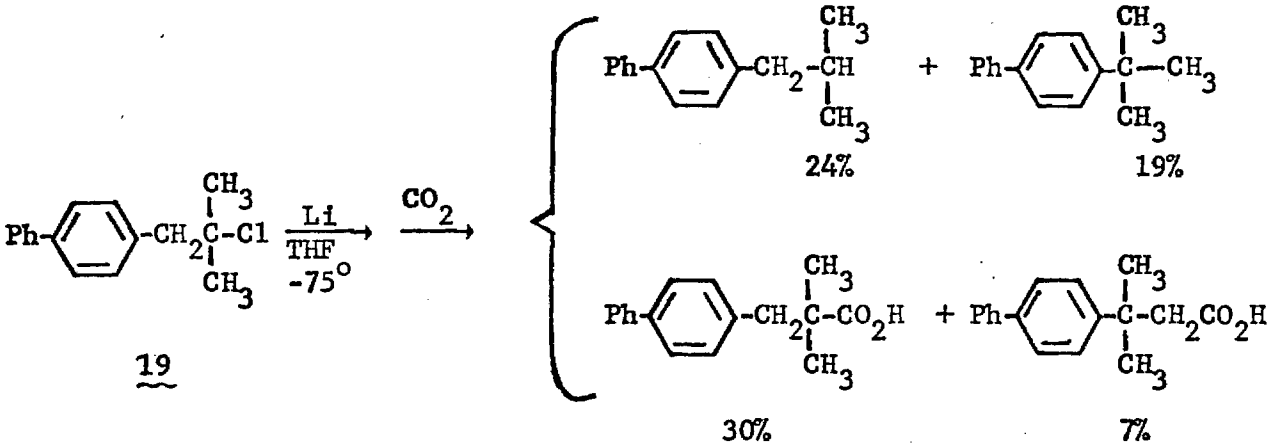
23 24 25

able to stablize the spiro anion relative to the open anion 23.

The reaction of halides 16 and 19 with lithium metal in tetrahydrofuran at -75° is of interest. The results are summarized below. The amount of rearrangement for



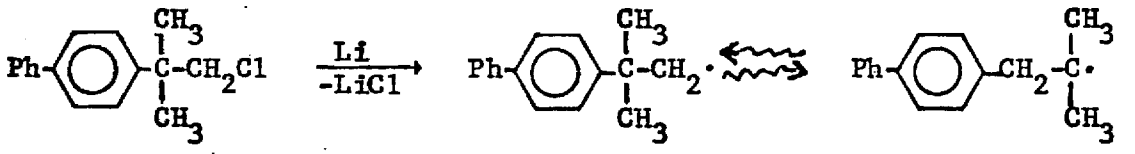
16



19

[8] D. J.Cram, "Fundamentals of Carbanion Chemistry," Academic Press, Inc., N.Y., N.Y., 1965, Chapter I.

reaction of halides 16 and 19 with lithium did not increae with increase in reaction time nor did the amount of rearrangement from halide 16 increase with increase in reaction temperature as shown by analyses for the volatile products listed in the above reaction summaries. Also when the reactions of halides 16 and 19 with lithium were run in THF containing a little tert-butyl alcohol the amount of rearrangement was not appreciably reduced. The organolithium compounds from chlorides 16 and 19 do NOT rearrange upon standing and the rearrangements observed are not rearrangements of carbanions but evidently rearrangements of free radicals formed during reaction at the lithium surface, e.g.



Other examples of rearrangements of radicals during reactions of organic chlorides with lithium metal have been reported[9] from our laboratories.

3. [1,2] Migration of Phenyl during Preparation of Grignard Reagents

In experiments directed toward preparation of an authentic sample of acid for use as a standard in the analysis of products from rearrangement of an organoalkali metal compound, we discovered that a phenyl group migrates partially during the preparation of the Grignard reagent from 5-chloro-4,4-diphenyl-1-pentene. In fairly extended studies phenyl groups were also found to under [1,2] migration during preparation of Grignard reagents from 2-chloro-1,1,1-triphenylethane and 1-chloro-2,3,4-triphenylpropane. The Grignard reagent itself once prepared from these halides does not undergo detectable rearrangement. The observed phenyl migration, therefore, occurs during formation of the Grignard reagent, likely by way of radicals formed at the surface of the magnesium metal just as we have observed for reactions of chlorides with lithium metals. Our results on phenyl migration during preparation of Grignard reagents have now been published in detail[10].

4. [1,2] Migrations of Phenyl and Acetylene Groups in Reactions of 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-pentyne and 5-Chloro-4,4-diphenyl-2-pentyne with Alkali Metals

While [1,2] rearrangements of vinyl groups in organoalkali compounds and Grignard reagents have been known for some time[11], corresponding migrations of acetylene groups have not been reported. We have found that 5-chloro-4,4-diphenyl-2-pentyne (26) reacts with lithium metal at -78° to give the expected organolithium product 27 which undergoes

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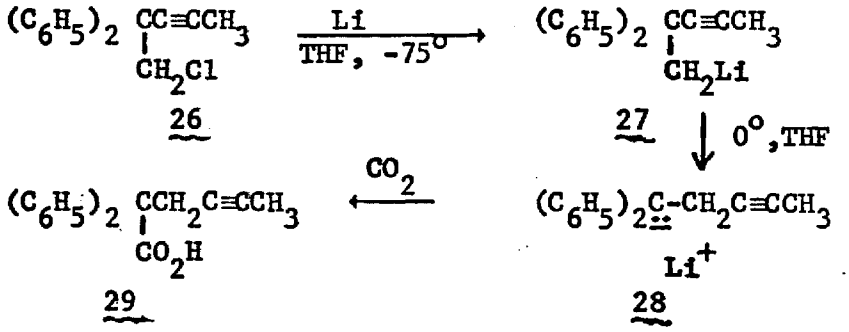
E. Grovenstein and Y.-M. Cheng, Chem. Commun., 101 (1970); E. Grovenstein, Jr., and J.-U. Rhee, J. Am. Chem. Soc., 97, 769 (1975).

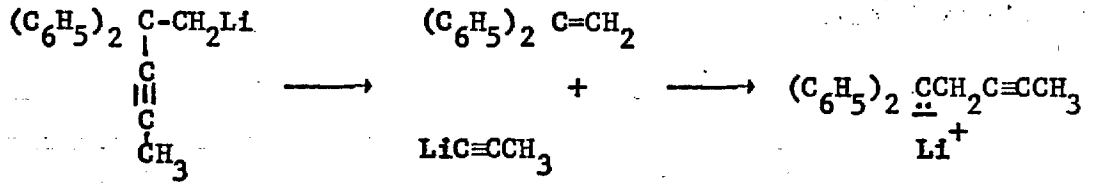
[10] E. Grovenstein, Jr., A. B. Cottingham, and L. T. Gelbaum, J. Org. Chem., 43, 3332 (1978).

[11] E. Grovenstein, Jr., Angew. Chem. Int. Ed. Eng., 17, pp 320-323 (1978).

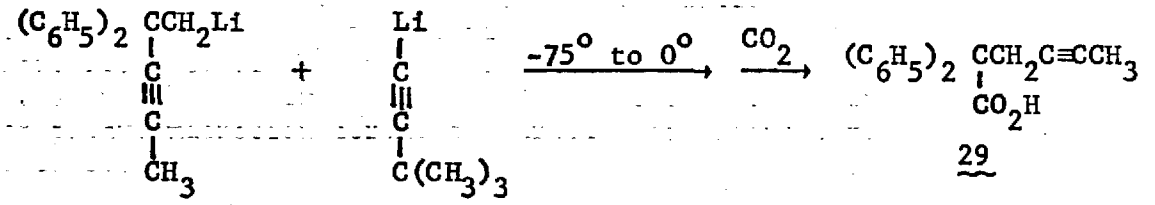


[1,2] migration of the $-C\equiv CCH_3$ group upon warming to 0° to give 28 which was characterized by carbonation to yield 29.

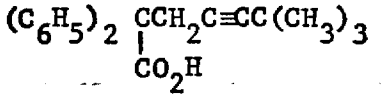
One possible mechanism for rearrangement of 27 would be by an elimination-readdition process outlined below:



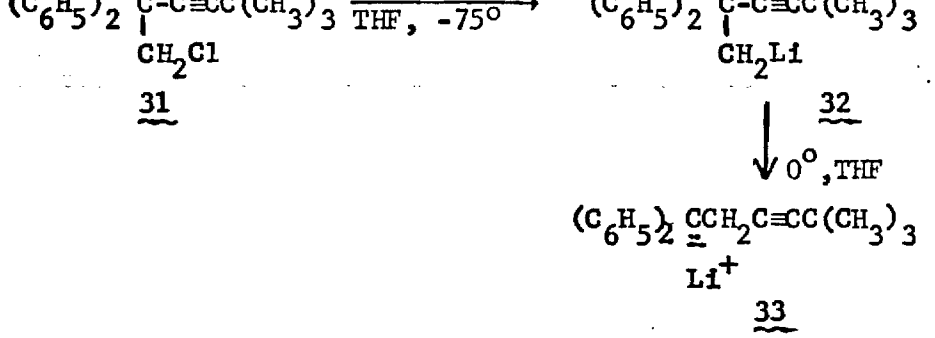
If the above mechanism were valid, it should be possible to intercept the intermediate diphenylethylene with another organolithium reagent such as $LiC\equiv CC(CH_3)_3$. Hence the test below has been carried out:



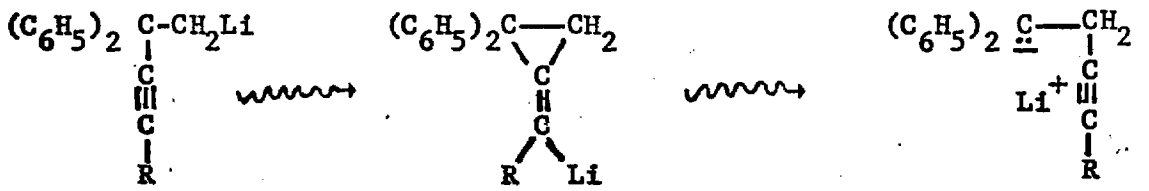
However, only the usual rearrangement product 29 was obtained and none (<1%) of the t-butylacetylene-incorporation product 30 could be detected.



That indeed a t-butylacetylene group is able to under a [1,2] rearrangement like the methylacetylene group of 27 was demonstrated by preparation and rearrangement of 32 to 33 under conditions analogous to those used for 27.

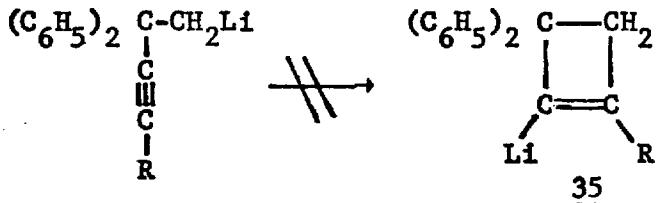


The most likely mechanism for the observed [1,2] migration of the acetylene groups in our organolithium compounds is by way of intermediate 34. This mechanism is



34

analogous to that accepted for migration of vinyl and aryl groups; however, the ring closure to 34 is an example of an 3-exo-digonal process which is disfavored by Baldwin's rules[12]. These rules would favor instead the 4-endo-digonal ring closure to 35 which, however, would not appear capable of leading to the observed products 28 and 33.

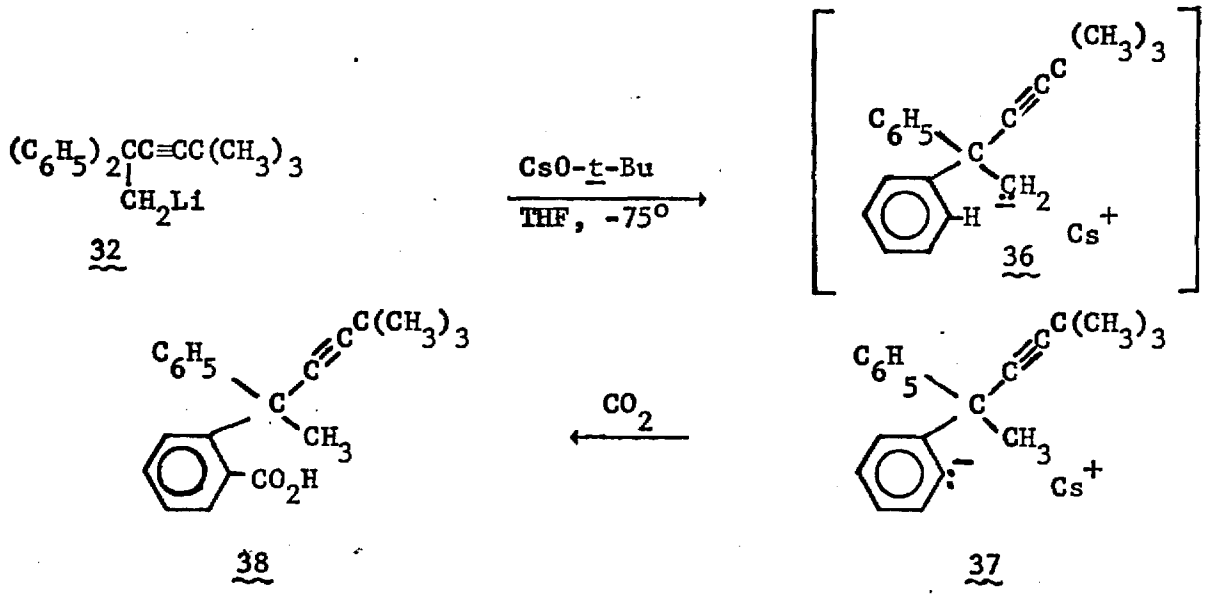


35

To probe the role played by the lithium cation in the above rearrangements of acetylene groups the organolithium compound 32 was treated with CsO-t-Bu at -75° with the aim of making the corresponding organocesium compound according to the general metathetical process shown in the following equation:

$$RLi + CsO\text{-}t\text{-}Bu \rightarrow RCs + LiO\text{-}t\text{-}Bu$$

In fact CsO-t-Bu catalyzed a new rearrangement of 32 evidently to the ortho metallation product 37. The structure of 37 rests the spectroscopic properties of its product of

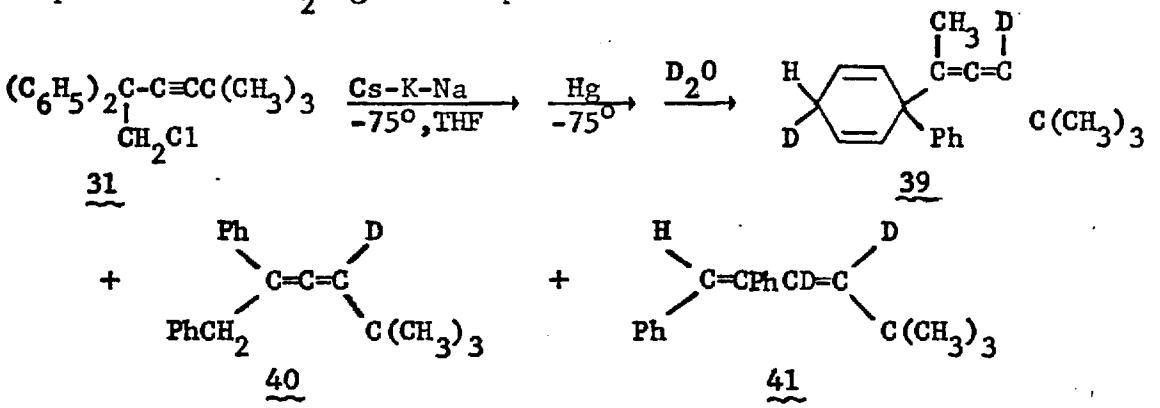


32 — 36 — 38 — 37

[12] J. E. Baldwin, J. Chem. Soc. Chem. Comm., 734 (1976).

carbonation 38; while the structure of 38 is likely correct, in view of some results with Cs-K-Na alloy described below, it needs confirmation.

The putative organocesium compound 36 was made also by reaction of the corresponding chloride 31 with Cs-K-Na alloy at -75°; treatment with mercury to remove excess alloy and decomposition with D_2O gave the products shown below.

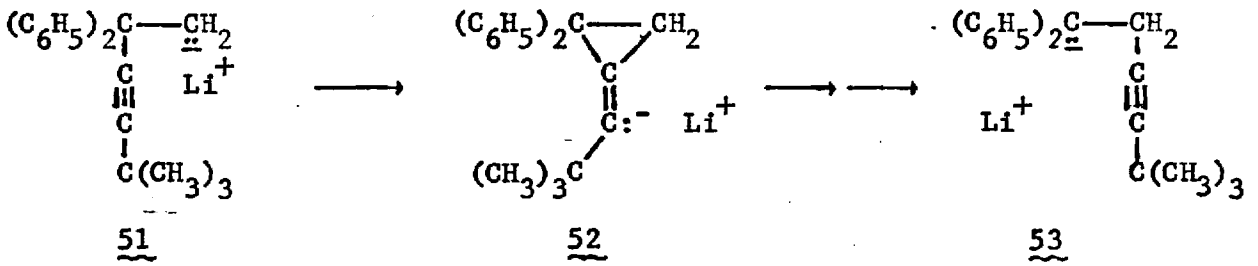


31 → 39 + 40 + 41

The ratio of 39:40:41 was approximately 40:30:30.

The products 39-41 may be accounted for by Scheme 1 (see page 12a). The organocesium compound 42 is given the same structure as that 36 formed by way of the corresponding organolithium compound 32. Yet 42 and 36 give different products! This is explained on the basis that 36 is formed initially as a solvent separated or loose ion pair; therefore, 36 is highly reactive and stabilizes itself by interaction with the nearest acidic proton which happens to be one in an ortho position of the two neighboring phenyl groups. Organocesium compound 42 formed by reaction of the chloride 31 with cesium alloy is evidently formed initially as a tight ion pair (contact ion pair). Species 42 is therefore longer lived than 36 and survives long enough to under [1,2] migration of the phenyl group or to extract a proton from anion 43 or from the solvent. It is notable that whereas the organolithium compound 32 undergoes only [1,2] migration of the acetylene group, the organocesium compound 42 undergoes only [1,2] migration of the phenyl group. That cesium as counter cation tends to favor migration of phenyl over other groups relative to lithium as counter cation has now been demonstrated in three cases: phenyl versus benzyl migration[13], phenyl versus allyl migration[14], and the present phenyl versus acetylene migration.

Our explanation for the cation effect upon the present rearrangements is that organolithium compound 32 rearranges in a tight ion pair via species 51 and 52 to the delocalized product 53. The reason why the tight ion pair with lithium (51)

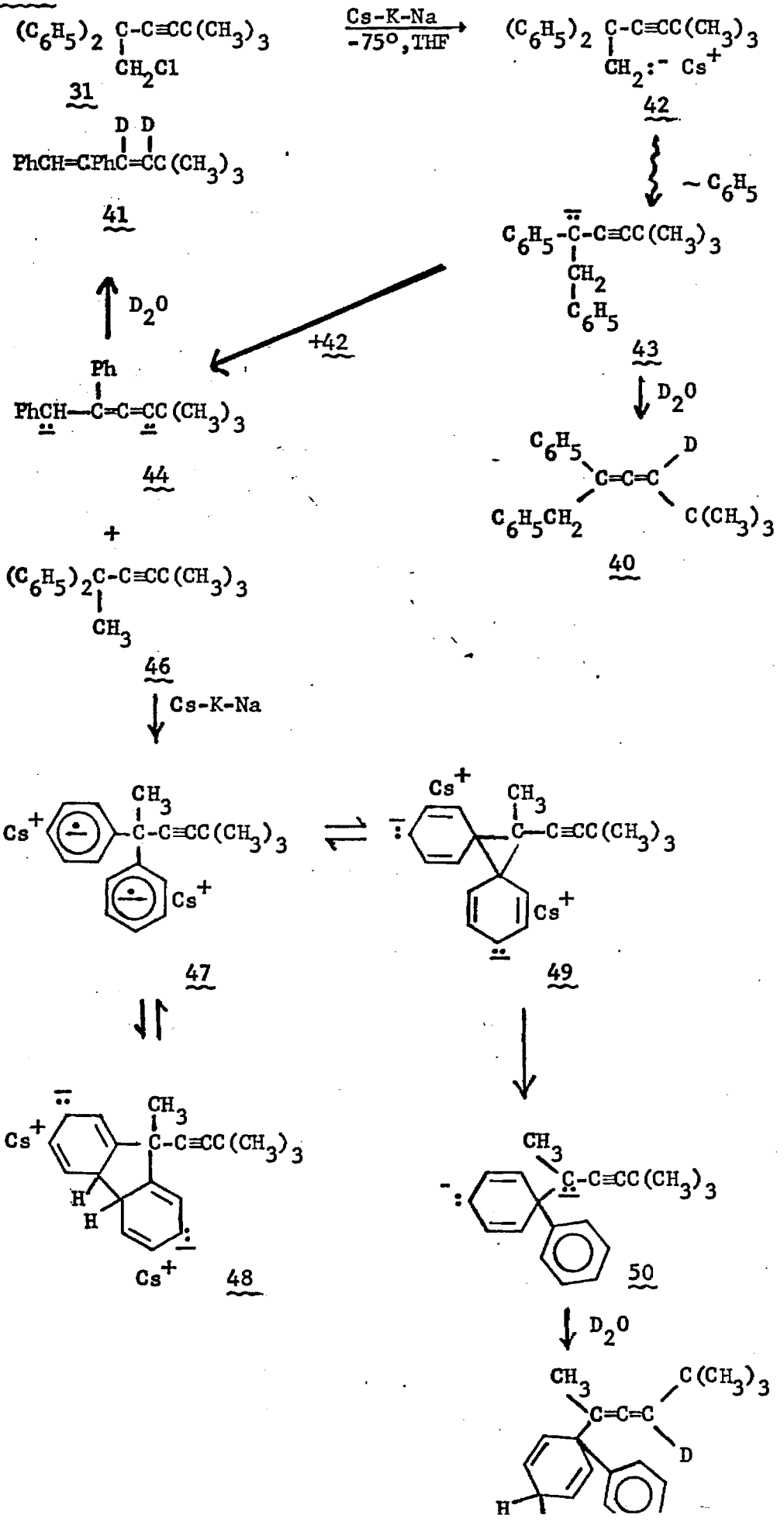


51 → 52 → 53

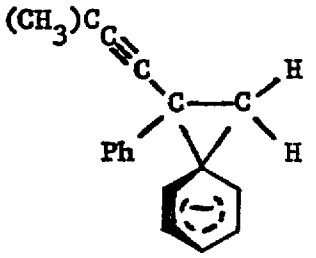
[13] E. Grovenstein, Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975).

[14] E. Grovenstein, Jr., and A. B. Cottingham, J. Am. Chem. Soc., 99, 1881 (1977).

Scheme 1



gives migration of the acetylene group whereas the tight ion pair with cesium (42) gives migration of the phenyl group depends upon the fact that lithium cation has an ionic radius (0.60Å) about the size of the covalent radius of carbon (0.77Å) whereas cesium cation has an ionic radius (1.69Å) about the size of the radius of a benzene ring (1.40Å for the ring of carbon nuclei). The net result of electrostatic and other forces of attraction between these alkali metal cations and their gegen anions appears to be that small lithium cations interact better with localized anions as in 51 and 52 than with delocalized anions such as 53 (which



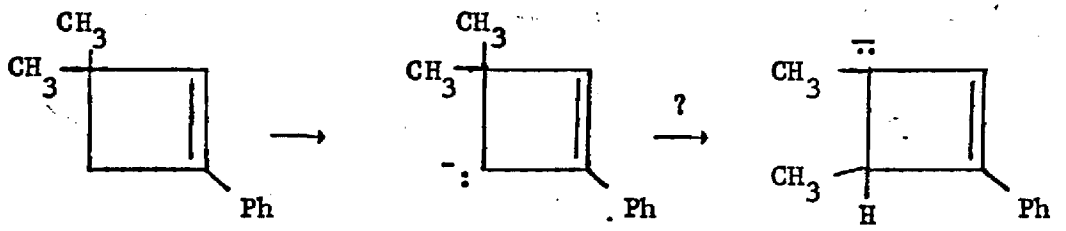
53

is the intermediate or transition state for phenyl migration) whereas large cesium cations interact better with the large delocalized anion 53 than with the localized anionic charge of 51 and 52.

The origin of product 39 as shown in Scheme 1 is highly speculative and without clear precedent. We suggest that it proceeds from the hydrocarbon 46 formed by protonation of 42. Clearly this suggestion is in need of confirmation. By analogy with other work[15] hydrocarbon 46 would be expected to give the dianion 48. Perhaps 48 is reversibly formed as shown in the reaction scheme. The final result, however, is that 46 gives 50 via a novel [1,2] migration of phenyl into an aromatic ring. This ususual rearrangement is clearly worthy of additional study as are other aspects of Scheme 1 such as the stereochemistry of diene 41 and its detailed mode of formation.

D. Search for [1,2] Migration of Methyl in Cyclobutenyl Anions

Previous unpublished work in our laboratory had as its goal study of possible [1,2] migration of methyl in the anion 55 whose synthesis was sought via reaction of olefin 54 with strong bases. This goal was frustrated by various alternative reactions, addition



54 55 56

of the base (e.g. n-butyllithium + tetramethylethylenediamine to the olefinic bond and possible metallation of the vinylic position or the aromatic ring of 54.

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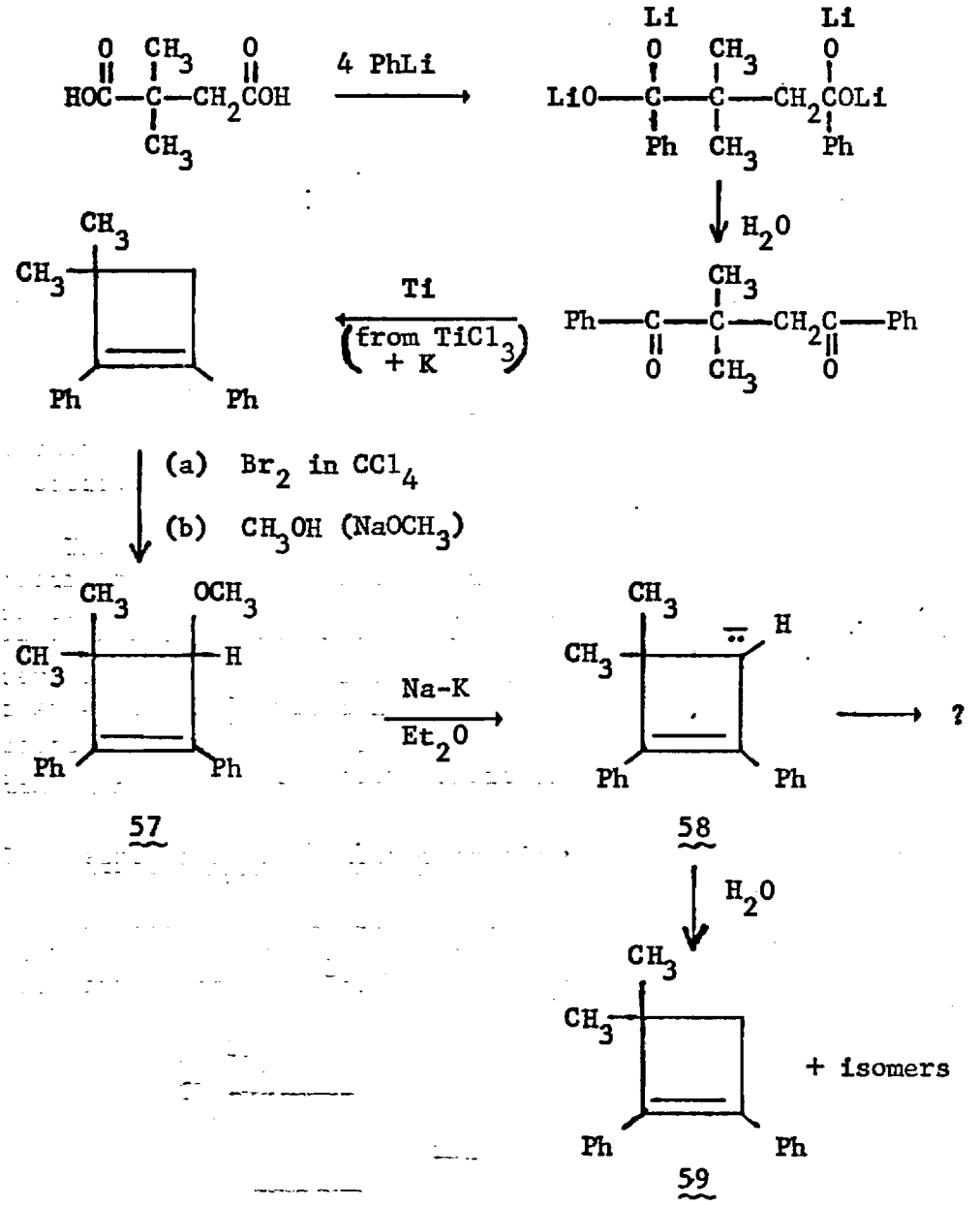
15 E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, J. Org. Chem., 37, 1281 (1972).

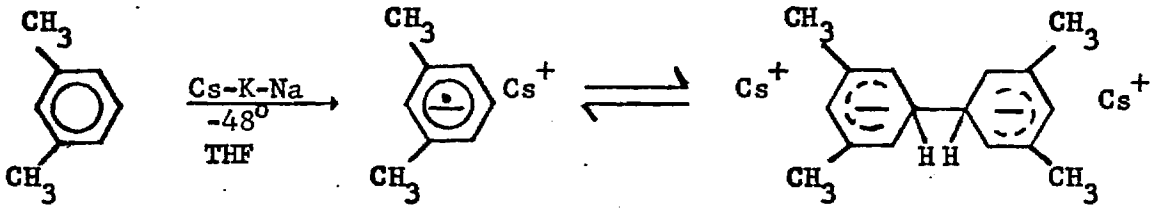
In new work the vinylic hydrogen of 54 and 55 has been replaced by a phenyl group which should both make vinylic metallation impossible and increase the stability of the allylic anion 55. Also the allylic anion has been sought by ether cleavage of 57 with alkali metals rather than by metallation. The following synthesis of 58 has been successfully achieved. At this state the composition of the olefinic mixture



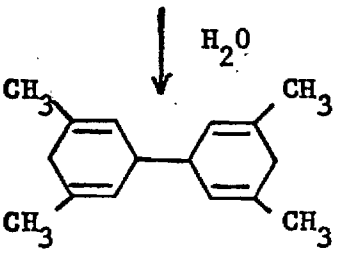
from protonation of the carbanion(s) has not been resolved save that one of the products appears to be the expected 59.

PART II. Reactions of Cesium and Cesium Alloys with Aromatic Hydrocarbons

Our work upon reaction of cesium and Cs-K-Na alloy with benzene and toluene has now been published[16] and, therefore, will not be discussed further here. In similar manner m-xylene reacts with excess Cs-K-Na alloy in THF at -48° to give the radical anion 60 which largely dimerizes to 61 as judged by the dimeric hydrocarbon 62 which is obtained in 55% yield as a beautifully crystalline compound upon siphoning the reaction mixture into ice water.

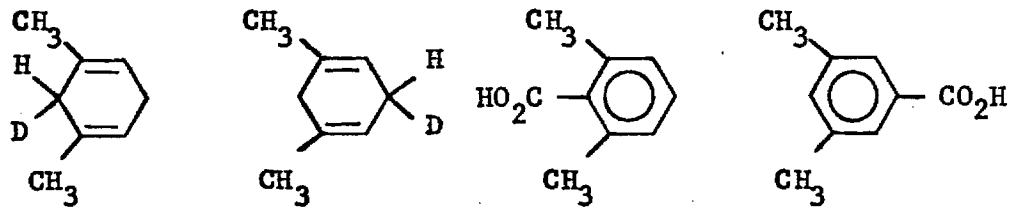


60 61



62

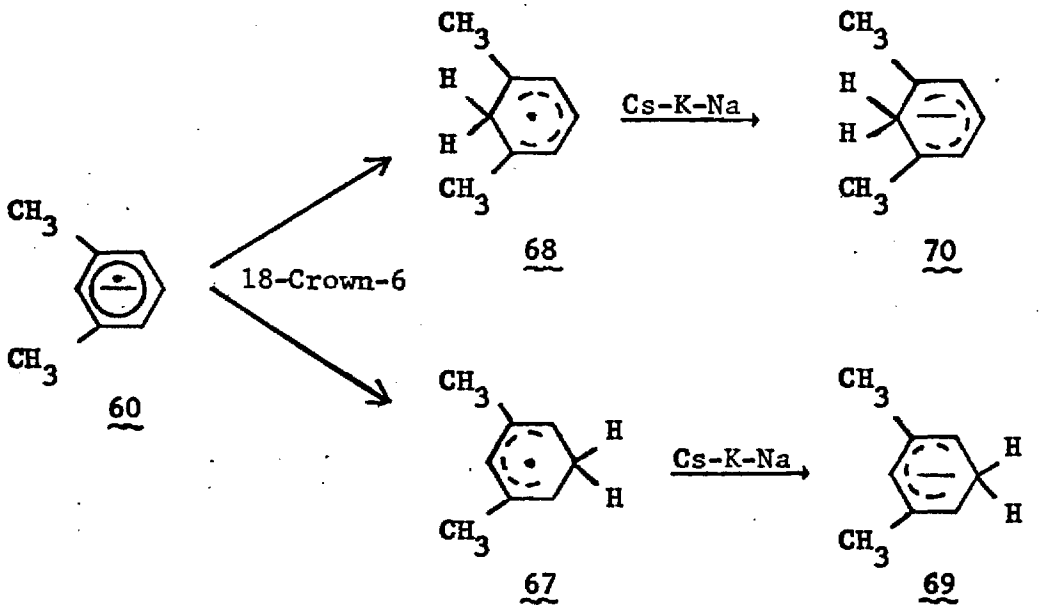
In contrast reaction of m-xylene with Cs-K-Na alloy in THF in presence of one molar equivalent of 18-Crown-6 gave on protonation after some three hours only monomeric hydrocarbons. For a reaction which was quenched with D_2O, 64 mole % of 2,5-dihydro-m-xylene and 33 mole % of unreacted m-xylene was obtained. According to ^1H and ^{13}C NMR analysis, the 2,5-dihydro-m-xylene was monodeuterated and consisted of a 1 : 3.74 ratio of 63 to 64. In another run with two molar equivalents of 18-crown-6 per mole of m-xylene, the acidic product from carbonation and dehydrogenation consisted of a 1: 3.86 ratio of 65 to 66. These data are in good argeement with the



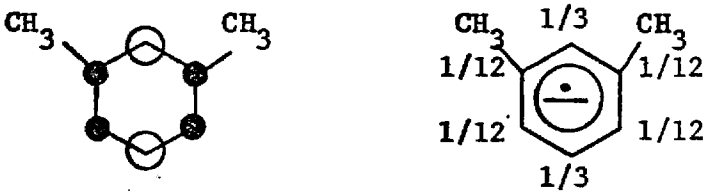
63 64 65 66

conclusion that 18-Crown-6 protonates the radical anion 60 to give about a 1 : 3.8 mixture of radicals 67 : 68 which are reduced to the corresponding ratio of anions 69 : 70.

16 E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).



Note that the chemistry of m-xylene radical anion can be interpreted in terms of the HOMO structure 71 or the charge distribution 72[17]. Dimerization and protonation



71 72

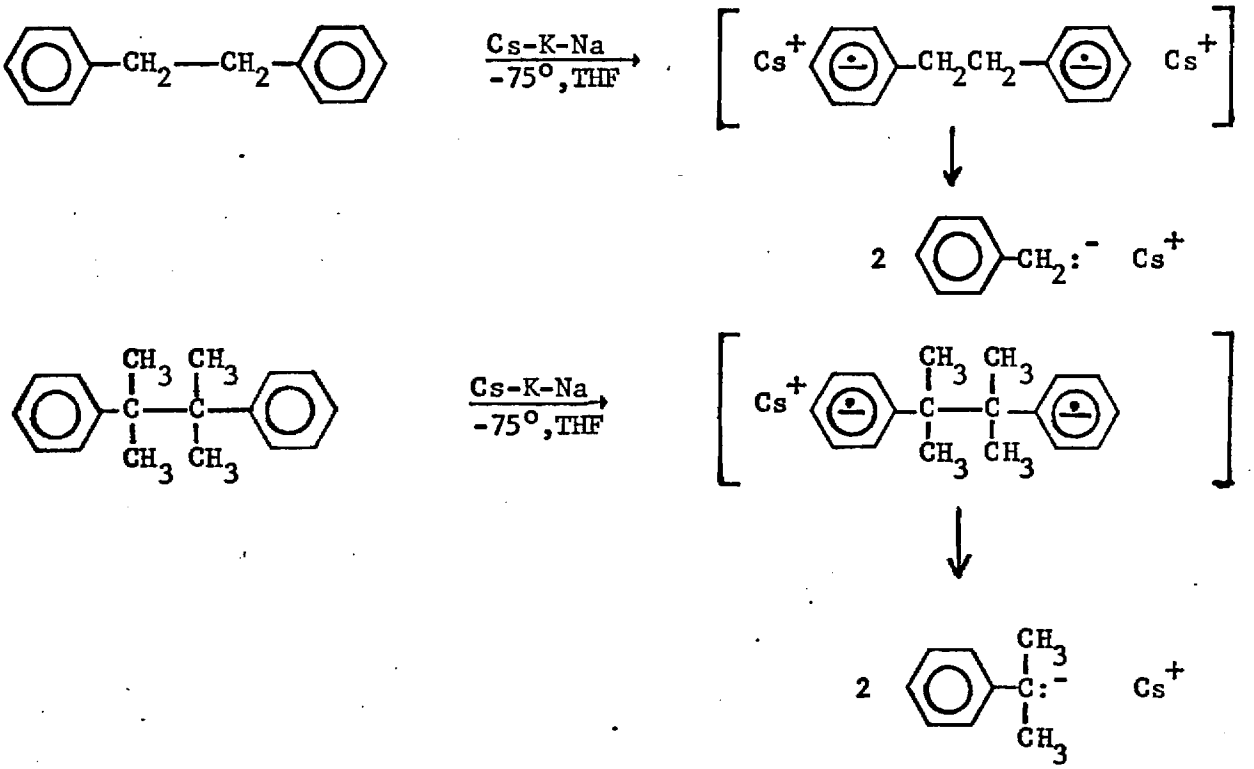
of the radical anion would be expected to take place at the positions of highest electron-spin density or charge density, hence at positions 2 or 5. Dimerization takes place preferentially at the 5 positiion since this process leads to the most stable anion 61 where the methyl groups are at the nodal positions in the HOMO (and hence destabilize the anions as little as possible). Protonation in contrast occurs preferentially at the 2-position since this process leads to the most stable radical 68 where the methyl groups are all at centers of high spin density (and hence stabilize the radical as much as possible). The higher regiospecificity in dimerization than in protonation accords with the larger effect of methyl groups in destabilizing anions than in stabilizing radicals in solution. The theoretical explanation of this substituent effect is poorly understood but the effect is of considerable importance to free radical and carbanion chemistry.

In similar experiments with benzene and Cs-K-Na alloy in THF at -43° in presence of two molar equivalents of 18-Crown-6 for five hours, the products of carbonation indicated that somewhat less than half of the benzene radical anion was protonated by 18-Crown-6 in contrast to complete protonation of m-xylene radical anion under

[17] See L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, N. Y., N. Y., 1966, p. 255.

milder conditions. These comparative results may be understood on the basis that methyl groups destabilize radical anions and increase their rate of protonation by 18-Crown-6.

The cleavage reactions shown below have been observed to take place readily at low temperature likely by way of intermediate dianions. The yields of benzylic anions



are quantitative. These reactions would appear to be of synthetic utility.

PART III. Publications of Work Supported by the Present National Science Foundation Grant

(1) "Carbanions. 17. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," E. Grovenstein, Jr., and A. B. Cottingham, J. Am. Chem. Soc., 99, 1881 (1977).

(2) "Carbanions. 18. Spiro Anions from Reactions of 2- and 3-p-Biphenylylalkyl Chlorides with Cesium-Potassium-Sodium Alloy," J. A. Bertrand, E. Grovenstein, Jr., P.-C. Lu, and D. VanDerveer, J. Am. Chem. Soc., 98, 7835 (1976).

(3) "Carbanions. 19. Reactions of Cesium or Cesium-Potassium-Sodium Alloy with Benzene and Toluene," E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).

(4) "Aryl Migrations in Organometallic Compounds of the Alkali Metals," by E. Grovenstein, Jr., in Advances in Organometallic Chemistry, F. G. A. Stone and R. West, Editors, Academic Press, New York, N. Y. Vol. 16, pp 167-210 (1977).

(5) "Phenyl Migration during Preparation of Grignard Reagents," E. Grovenstein, Jr., A. B. Cottingham, and L. T. Gelbaum, J. Org. Chem., 43, 3332 (1978).

(6) "Skeletal Rearrangements of Organoalkali Metal Compounds," E. Grovenstein, Jr., Angew. Chem., 90, 317-336 (1978); Angew. Chem. Int. Ed. Engl., 17, 313-332 (1978).

wo Ph.D. theses have been completed under the present grant:

Pang-Chia Lu, "Spirocyclic Intermediates in the Rearrangements of Organoalkali Compounds," Ph.D. Thesis, Georgia Institute of Technology, September, 1977.

Dean E. Quest, "Reactions of Cesium Alloys with Aromatic Hydrocarbons and Alkyl Chlorides," Ph.D. Thesis, Georgia Institute of Technology, October, 1977.

ıile preliminary communications have been published on both of the above theses, that f Lu is currently being written up in full detail. The work of Quest is being ıtended and will be published in detail following completion.

G-33-610

PROPOSAL TO THE NATIONAL SCIENCE FOUNDATION
Cover Page

FOR CONSIDERATION BY NSF ORGANIZATIONAL UNIT (Indicate the most specific unit known, i.e. program, division, etc.)	IS THIS PROPOSAL BEING SUBMITTED TO ANOTHER FEDERAL AGENCY? Yes ___ No X ; IF YES, LIST ACRONYM(S):
Chemistry Division Chemical Dynamics Program	

PROGRAM ANNOUNCEMENT/SOLICITATION NO.:	CLOSING DATE (IF ANY):

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Georgia Tech Research Institute

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225 North Avenue, N. W., Atlanta, Georgia 30332

TITLE OF PROPOSED PROJECT

"Cation Effects in Organoalkali Metal Chemistry; Organocesium Chemistry"

REQUESTED AMOUNT	PROPOSED DURATION	DESIRED STARTING DATE
$278,127	Four Years	July 1, 1980

PI/PD DEPARTMENT	PI/PD ORGANIZATION	PI/PD PHONE NO.
School of Chemistry	Georgia Institute of Technology	404: 894-4049

PI/PD NAME	SOCIAL SECURITY NO.*	DATE OF HIGHEST DEGREE ACHIEVED	MALE*	FEMALE*
Erling Grovenstein, Jr.	256-32-1870	1948, Ph.D.	X	
ADDITIONAL PI/PD				
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DATE January 15, 1980	DATE 1/15/80	DATE 1-15-80

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225 North Avenue, N.W., Atlanta, Georgia 30332

3. PRINCIPAL INVESTIGATOR AND FIELD OF SCIENCE/SPECIALTY

Erling Grovenstein, Jr.
(Organic Chemistry)

4. TITLE OF PROJECT

"Cation Effects in Organoalkali Metal Chemistry; Organocesium Chemistry"

5. SUMMARY OF PROPOSED WORK (LIMIT TO 22 PICA OR 18 ELITE TYPEWRITTEN LINES)

The purpose of this research is to study cation effects in organoalkali metal chemistry and in particular to develop an organometallic chemistry of cesium for comparison with that of lithium. One major topic concerns variation of migratory aptitudes of groups in organoalkali rearrangements as the counter cation is varied from lithium to cesium to potassium-18-crown-6. The systems to be studied here are compounds in which there is competitive migration of alkynyl and vinyl versus phenyl groups and competitive [3,3] versus [2,3] sigmatropic rearrangements. A second major topic is that of the almost unique reactions of hydrocarbons with cesium; these include addition of cesium to alkylbenzenes to give rather stable monomeric and dimeric products, reaction of cesium with ethylene and 2,2,5,5-tetramethyl-3-hexyne, cleavage of carbon-carbon and carbon-hydrogen bonds by cesium, and skeletal rearrangements of unsaturated hydrocarbons induced by cesium. It is hoped that these studies will lead to some understanding of why cesium has an organometallic chemistry so different from that of lithium. Toward this end the studies will delve into the mechanisms of these reactions, the role of solvents and ligands about the alkali metal cation, and a search for intermediates.

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CATION EFFECTS IN ORGANOALKALI METAL CHEMISTRY; ORGANOCESIUM CHEMISTRY

Introduction

Organoalkali metal compounds are frequently referred to as "carbanions" by organic chemists who are chiefly concerned with utilizing these compounds in construction of new carbon frameworks. This organocentric view ignores the relevance of the counter cation which in conjunction with the solvent (or other ligands such as crown ethers) can greatly modify both the physical and chemical properties of an organoalkali metal compound.

The role of the counter cation and solvent in altering the properties of delocalized carbanions has been studied in pioneering studies especially of Michael Szwarc, J. Smid, T. E. Hogen-Esch, E. Warhurst, R. Waack, J. F. Garst, T. L. Brown, and their collaborators[1]. From these studies the idea has arisen that organoalkali metal compounds in ethereal solvents can exist as tight or contract ion pairs ($R:^-M^+$), loose or solvent-separated ion pairs ($R:^-||M^+$), as free ions ($R:^- + M^+$), as various ionic aggregates such as triple ions ($R:^-M^+R:^-)(M^+R:^-M^+$) or higher polymers $(R:^-M^+)n$, and, in principle, as covalent molecules RM or (RM)n. Schlosser[2] has noted that the distinction between a contact ion pair and a covalent molecule is ill defined especially in light of the fact that most covalent bonds have partial ionic character. Also it should be noted that all tight ion pairs ($R:^-,M^+$) do not have the same degree of tightness since this varies with the size of the cation M^+ with the result that large cations may be as loosely bound to anions as small solvent-separated cations. Also many of the properties of free ions are similar to those of loose ion pairs.

While the chemical and physical properties of solutions of organoalkali metal compounds with delocalized anions are now moderately well understood, much less is known about the chemistry of organoalkali compounds where the charge may be considered to be localized on a single carbon atom in a ground state or in a transition state. Partial exception to this generalization must be made for organolithium compounds which are now commercially available and have helped revolutionize modern synthetic organic chemistry. It is a major thesis of this research proposal that the other alkali metals sodium, potassium, rubidium, and cesium should have much to contribute to both practical and theoretical organic chemistry. Since the family of alkali metals from lithium to cesium form a graded series in which their properties change in a regular or periodic fashion with atomic number, sodium should be most similar to lithium and cesium least similar in its organometallic chemistry. Hence in our exploratory research we propose to concentrate our studies on organocesium chemistry and, for comparison sake, where necessary examine the corresponding organolithium chemistry. We recognize, of course, that this abbreviated path of research may overlook much unique chemistry for the other alkali metals. Hopefully our program of research will point the way to where such unique chemistry may be expected.

Why might organolithium and organocesium compounds be expected to be very different and why might these differences be of importance to chemistry? The most obvious difference is that lithium is much smaller than cesium, thus Pauling's ionic radii are 0.60 and 1.69Å for lithium and cesium cations respectively or their corresponding single-bond metallic radii are 1.23 and 2.35Å. This means that toward an anion with a localized negative charge, Li^+ should be bound more tightly by electrostatic attraction than Cs^+ provided that both ion pairs exist as contact ion pairs.

Solvation can alter this result; the solvated lithium cation in a solvent-separated ion pair has a radius[3] of about 4.5Å and thus is larger than an unsolvated cesium cation. The general tendency[3] is for the fraction of solvent separated ion pairs to increase along the series $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ in agreement with cesium ion having the smallest (63 kcal/mole) and lithium the largest (124 kcal/mole) heat of hydration[4]. Because of the complications of solvation it is frequently difficult to predict a priori whether lithium or cesium will be more tightly bound to an anion by forces of electrostatic attraction.

Another difference between lithium and cesium is in the extent of covalent bonding to carbon. The experimental bond dissociation energies of diatomic alkali metal molecules M_2 decrease from 25.0 kcal/mole for lithium to 10.4 kcal/mole for cesium[4] while the corresponding alkali metal hydrides (as diatomic molecules) are estimated to have 80 and 85% partial ionic character respectively[5]. These numbers imply that while localized anions such as butyl anion are bound to alkali metal cations largely by Coulombic forces nevertheless the bonds have some covalent character especially for organolithium compounds. Unanswered are detailed questions such as whether or not cesium utilizes 5d orbitals to stabilize compounds such as cesium benzenide[6] and whether the differing polarizabilities of alkali metal cations are of importance in bonding. While considerable progress has been made in unraveling the structures of organolithium compounds[7], much remains to be learned in both fact and theory[8].

The energy[4] required to ionize a lithium atom in the vapor phase (124.2 kcal/mole) is considerably greater than that of cesium (89.7 kcal/mole). Both the higher ionization potential and smaller size of lithium contribute toward organolithium compounds being more covalent than organocesium compounds. The stronger solvation of lithium than cesium ions can "wash out" the difference in ionization potential; in aqueous solution the standard oxidation potentials of lithium and cesium are exactly the same (and not much greater than those of the other alkali metals). It is perhaps similarities such as this which have discouraged attempts to develop organocesium chemistry. We would note that in organic solvents (especially hydrocarbons but likely also ethers) the oxidation-reduction potentials of lithium versus cesium likely parallel vapor phase ionization potentials with cesium being a stronger reducing agent than lithium.

The above discussion of factors such as size, covalent versus ionic character, solvation, and aggregation make it clear that lithium and cesium are very different elements but it is hard to predict whether or not their organometallic chemistry is different enough to warrant detailed study of the less abundant element cesium. The summary (see APPENDIX I, Summary of Previous Work) of examples which are known to the chief investigator, however, makes it clear that the organometallic chemistry of these elements is in fact markedly and usefully different.

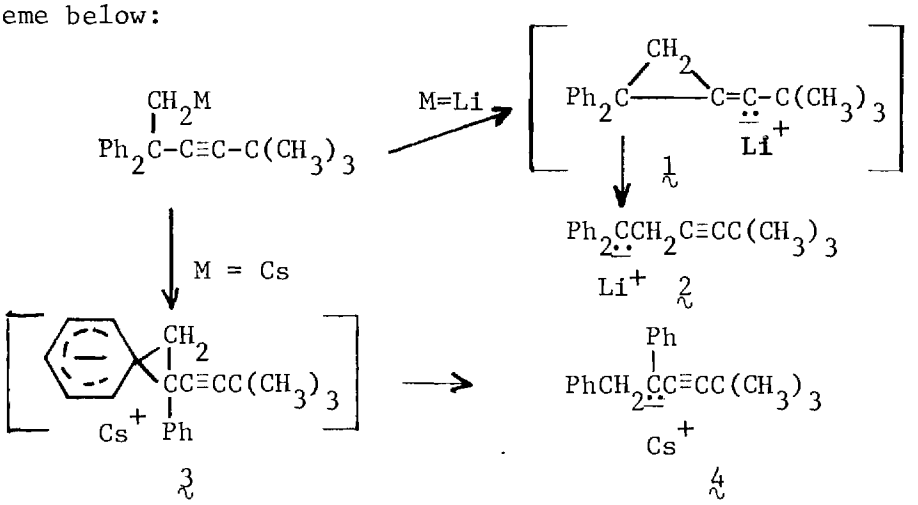
Suggested New Experiments

From the twelve areas summarized in APPENDIX I of alkali metal cation effects in organic chemistry, we have chosen two general topics for our proposed new work. Namely we wish to study the variation of migratory aptitudes of groups in organoalkali rearrangements with change of alkali metal cation (especially cesium versus lithium) and the general reactions of hydrocarbons which are almost unique with the metal cesium. It is hoped that these studies will lead to some understanding of why cesium has an organometallic chemistry so different from that of lithium. Toward this end the studies will delve into the mechanisms of the reactions, the role of solvent and ligands about the alkali metal cation, and a search for intermediates which may exist for at least a few minutes in tetrahydrofuran solution at the temperature of a Dry Ice bath.

1. Variation of Migratory Aptitudes of Groups in Organoalkali Rearrangements as the Counter Cation Varies from Lithium to Cesium to Potassium-18-Crown-6.

(a) Alkynyl versus Phenyl Migration

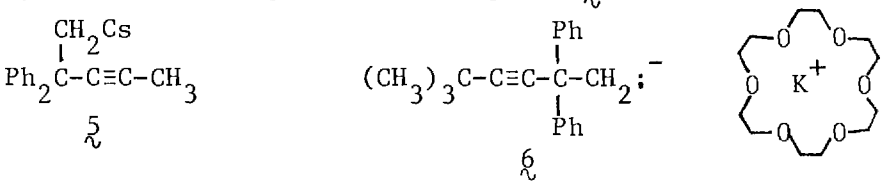
The preferential [1,2] migration[22] of an alkynyl group with lithium as counter ion but of a phenyl group with cesium as counter ion may be analyzed in terms of the mechanistic scheme below:



1 2 3 4

If the results of CNDO/2 calculations[46] can be accepted[8], carbanion 3 is some 8 kcal/mole more stable than carbanion 1 (in absence of interactions with counter cation and solvent). A cesium cation would be expected to stabilize the two anions approximately equally, perhaps somewhat favoring 3 because of its less hindered steric environment and greater polarizability. A lithium cation in contrast evidently stabilizes 1 appreciably more strongly than 3 in agreement with the cumulating evidence (see Appendix I, "Summary of Previous Work") that a lithium cation can interact more strongly with a localized than with a delocalized charge, likely because of the appreciable covalent character of many carbon-lithium bonds. Additional experiments need to be done to confirm this interpretation.

The less sterically incumbered organocesium compound 5 needs to be studied to affirm



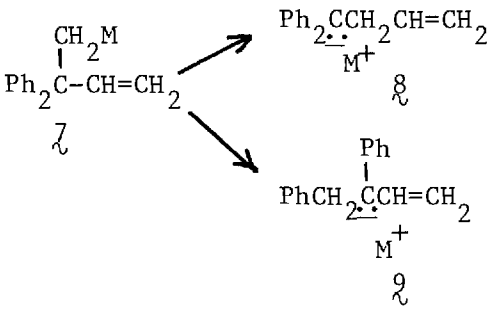
5 6

that migration of phenyl in the t-butyl compound was not the result of unfavorable steric interactions of the large cesium ion with the t-butyl group of 1. Also the potassium-crown ether complex 6 needs to be studied to show whether or not migration of an alkynyl group can be realized in such a loose ion pair. In terms of our theory given above migration of the alkynyl group should not occur in 6; however, migrations of benzyl[16] and allyl[17] groups in organolithium compounds occur in loose ion pairs analogous to 6 and lithium ion is known to be the most strongly solvated of the alkali metal cations. The potassium-18-crown-6 complex 6 will be generated from the corresponding chloride by reaction with potassium metal dissolved[47] in 18-crown-6 (18-C-6) in tetrahydrofuran and from the corresponding organolithium compound by reaction[16] with potassium t-butoxide complexed with 18-C-6.

(b) Vinyl versus Phenyl Migration

The same principles should be involved in vinyl migration as in alkynyl migration; hence further to establish and exemplify the theory we wish to study rearrangement of 7.

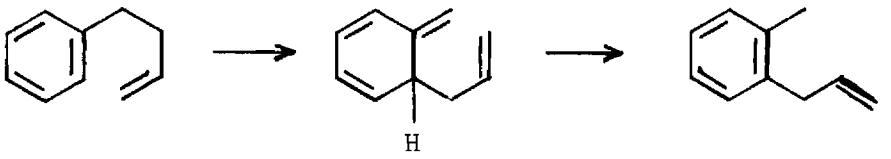
We would predict that for M = Li the product would be that of vinyl migration (8), for M = Cs that of phenyl migration (9), and for M = K -18-C-6 either phenyl migration or protonation of 7. While vinyl and phenyl migration in organometallic compounds have been known for some twenty years, the relative migratory aptitude of these groups appears never to have been tested in organoalkali metal compounds. In



organomagnesium compounds (Grignard reagents), migrations of vinyl groups are common while migrations of phenyl groups do not occur in ethereal solvents[48-50]. Migration of aryl groups other than phenyl may be possible in Grignard reagents since various pyridylalkyl-magnesium compounds have been observed to undergo spirocyclization and the reverse process[51].

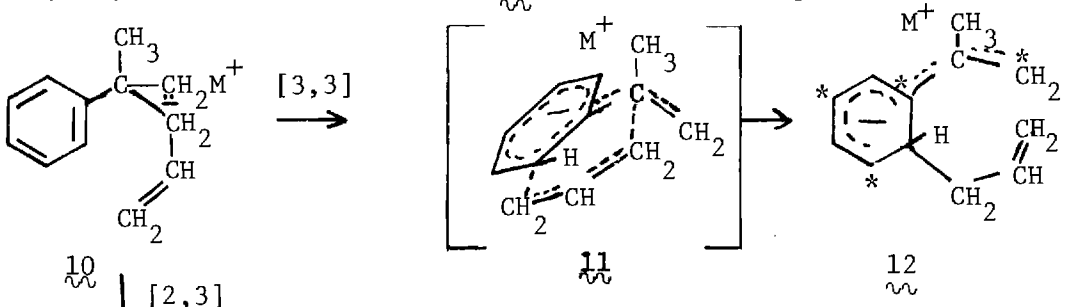
(c) Sigmatropic [3,3] versus [2,3] Rearrangement

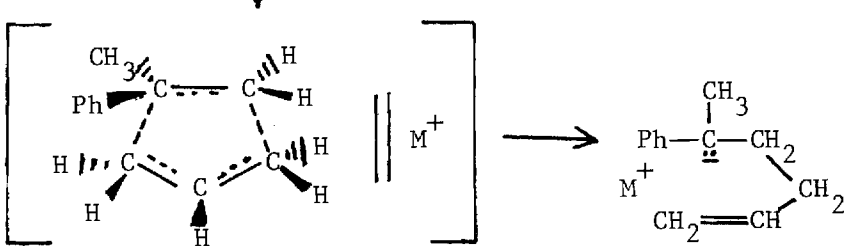
The aromatic Cope rearrangement or all-carbon Claisen rearrangement (eq. 15)



(15)

has never been observed (in the absence of the driving force from the relief of cyclopropane ring strain[52]) even as a minor process in a re-investigation with the benefit of modern methods of analysis[53]. In analogy to the great acceleration of the oxy-Cope [3,3] sigmatropic rearrangement observed by Evans and Golob[23] (see "Summary of Previous Work") on conversion of an alcoholic hydroxyl group into an alkoxide with a loosely bound alkali metal cation, we wish to see if the aromatic Cope rearrangement is subject to similar activation by a carbanionic charge with a counter cesium cation. Hence we wish to study rearrangement of 2-methyl-2-phenyl-4-pentenyl anion (10). The desired [3,3] sigmatropic rearrangement of 10 is expected to proceed by a transition state 11 whose driving force is the delocalization of negative charge to give finally the heptatrienyl anion 12. A likely competiting [2,3] sigmatropic rearrangement proceeds by way of a transition state 13 in which the negative charge is delocalized





over the five carbon atoms of the cyclic array but likely is largely concentrated in the bonding region between the ends of the allylic and ethylenic moities. A distinction between transition states 11 and 13 is that in 11 negative charge is becoming distributed as in the final planar heptatrienyl system 12 (see starred positions) and the cation is free to approach the negative charge on the side of the benzenoid ring anti to the attacking allyl group. In contrast in 13 while some of the negative charge is flowing into the aromatic ring as in the final benzylic anion 14, most of the charge is likely involved in bonding in the five-membered ring which contains a six-electron, "aromatic" or Hückel arrangement of electrons and the charge is shielded from close approach of the counter cation by the methyl, phenyl, and hydrogen atoms joined to the allyl and ethylenic moities. In agreement with this postulate of the charge distribution in the [2,3] anionic rearrangement, we note that the only well studied example[17] of this rearrangement occurs in a loose ion pair.

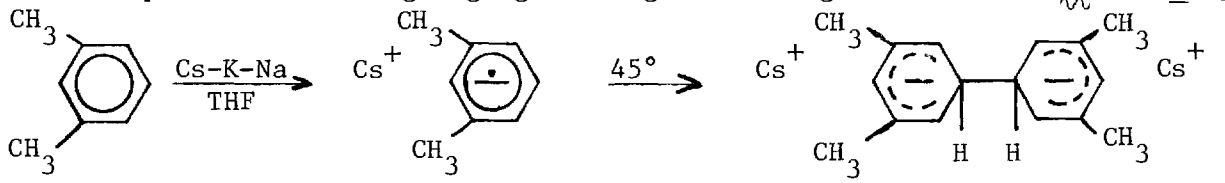
Hence we wish to study rearrangement of 10 with M^+ = Cs^+, Li^+, and K^+-18-C-6. We expect that with cesium as cation the major product will be the [3,3] sigmatropic arrangement product 12 while with lithium and potassium-18-C-6 the main product will be 14. The experiment with potassium ion complexed with 18-C-6 is being performed to check upon the interpretation of the lithium ion result which is otherwise always, ambiguous with respect to whether the observed reaction proceeds by a loose or a tight ion pair.

2. Reactions of Hydrocarbons with Cesium

Introduction[31a] of the ternary eutectic of cesium, potassium, and sodium of melting point -79° into organic chemistry has provided a facile means of generation or organocesium compounds at low temperatures since this alloy is somewhat soluble (blue solution) in tetrahydrofuran at -78° and selectively gives up cesium to benzenoid compounds[6] and alkyl chlorides[54]. Because of the low temperatures and short reaction times required, and occasionally because of the insolubility of organocesium compounds in tetrahydrofuran, highly reactive intermediate organocesium compounds can sometimes be characterized prior to conversion to more stable products. We desire to probe the utility of Cs-K-Na alloy in the areas delineated below.

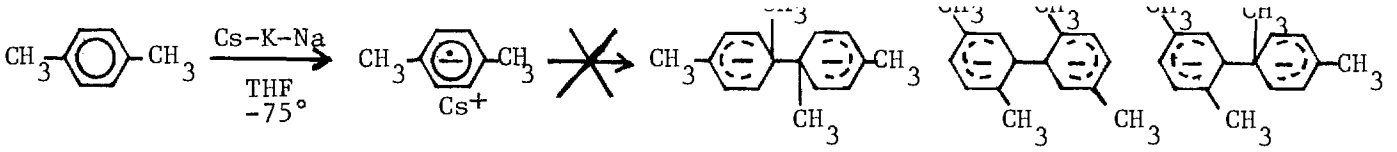
(a) Addition of Cesium to Alkylbenzenes; Monomeric and Dimeric Products

Illustrative of the capabilities of Cs-K-Na alloy is the first preparation[6] of cesium benzenide in synthetically useful quantities in THF at -70°. Toluene[6] and m-xylene[54] undergo similar reactions. Dimerization of the essentially insoluble anion radicals is slow at -70° but moderately rapid at -45° to give products in which methyl groups, if present, are oriented essentially exclusively at the nodal positions of the HOMO or the positions bearing negligible negative charge as shown in 16 for m-xylene.



15 16

In agreement with this view, p-xylene[55] gives an anion radical 17 but this radical does NOT dimerize at -45° since all likely dimeric products (18, 19, and 20) have two methyl groups on carbons bearing negative charge.



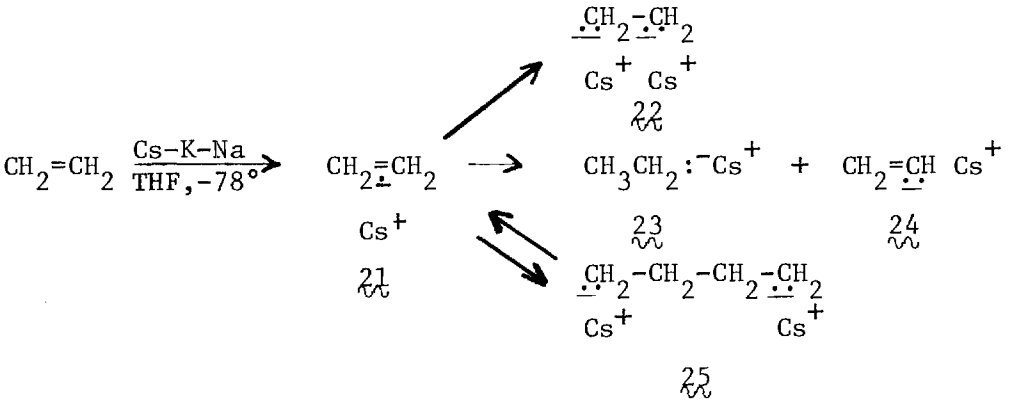
17 18 19 20

To test how general are reactions of Cs-K-Na alloy with alkylbenzenes and to probe the rule given above for dimerization of the resultant anion radicals we wish to study the reactions of ethylbenzene, isopropylbenzene, tert-butylbenzene, o-xylene, and mesitylene with Cs-K-Na alloy in THF at -75° and to look for possible products of dimerization at -45°. Will the results with cesium alloy parallel the peculiar equilibrium constants reported by Lawler and Tabit[56] for anion radical formation by alkylbenzenes with Na-K alloy in tetrahydrofuran-dimethoxyethane solution as measured by an esr technique?

Lawler and Tabit[56] noted that their results are not well accounted for simply by the "electron-donating" effects of alkyl groups. Solvation, ion pairing, and steric effects are likely to be of significance. For insoluble cesium compounds the lattice energy of the ionic array would also be of importance. To help disentangle some of these factors it would be of interest to compare reactions of Cs-K-Na alloy with anisole, N,N-dimethylaniline and trimethylsilylbenzene to those with hydrocarbons of similar size, namely ethylbenzene isopropylbenzene, and tert-butylbenzene respectively. Hence we will study reactions of these hetero-atom analogs of our hydrocarbons with Cs-K-Na alloy if time permits. Note that N,N-dimethylaniline is not reducible[57] to a radical anion by potassium in tetrahydrofuran-dimethoxyethane according to esr studies unless a stabilizing group such as nitro or trimethylsilyl is present. We would anticipate that at the high concentrations possible in our Cs-K-Na alloy reductions, the radical anion[58] of trimethylsilylbenzene would likely dimerize at the position para to the silyl group or otherwise such that much electron density was on the carbon attached to the silyl group in the dimer (opposite to the effect of a methyl group).

(b) Reaction of Cesium with Ethylene

Reports[35-37] of the reaction of cesium with ethylene are interesting, though inconclusive (see "Summary of Previous Work") and are likely complicated by successive reactions at the comparatively high temperatures and long reaction times employed. We would like to subject the reaction of ethylene with Cs-K-Na alloy to the same careful scrutiny we used for benzene[6] (chemical derivatization, esr studies, measurement of the amount of cesium combined with a known quantity of ethylene by study of the composition of the phases present, and changes of reaction products with time and temperature). Our preconceptions about the likely reactions of Cs-K-Na alloy with ethylene are shown in the scheme below:



21 22 23 24 25

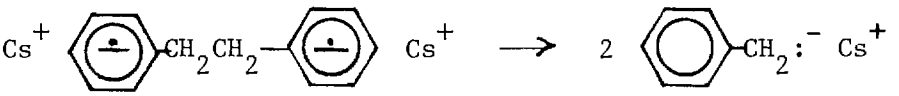
We envision that ethylene radical anion 21 is first formed; this could then be reduced to the dicesium adduct 22 as suggested by Hackspill and Rohmer[36]. Such a compound with negative charges on adjacent atoms violates Pauling's adjacent charge rule and seems improbable. Alternatively ethylene radical anion might disproportionate to ethylcesium (23) and vinylcesium (24) or dimerize reversibly to tetramethylene dicesium (25). The compound of Hackspill and Rohmer which yielded ethane upon addition of water might have been any of the compounds 21-25 or some combination of these. Obviously these compounds are capable of adding ethylene to give higher molecular weight hydrocarbons as reported by Clusius and Mollett[37].

(c) Reaction of Cesium with 2,2,5,5-tetramethyl-3-hexyne

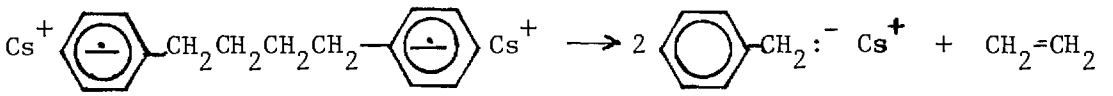
The reports that cesium combines with ethylene raises the question as to whether or not cesium can add to a triple bond to give an isolable adduct. Acetylene itself cannot be studied because of its known tendency to give alkali metal acetylides. Alkyl groups lower the reactivity of double bonds with cesium Thus propylene is much less reactive than ethylene toward cesium[37] and cis-2-keptene shows no detectable reaction[59] with Cs-K-Na alloy in THF at temperatures of -75 to 29°C. In contrast 3-hexyne reacts readily[60] to give mostly a monometallation product ($CH_3CH_2C{\equiv}C\dot{C}HCH_3$ Cs^+) and some dimetallation product. We think, therefore, it would be of interest to see if the acetylene 2,2,5,5-tetramethyl-3-hexyne which has no acidic hydrogen atoms will give a reac tion product with cesium metal or Cs-K-Na alloy in THF. Is a stable radical anion, dianion, or dimer of the radical anion formed?

(d) Cleavage of Carbon-Carbon Bonds by Cesium

We have discovered[61] that dibenzyl and many of its methyl derivatives are readily cleaved by Cs-K-Na alloy in THF at -75° as dianions according to the process:



We would like to test how general this reaction may be for other classes of compounds; thus may one or both of the phenyl groups of dibenzyl be replaced by vinyl, acetylene, or nitrile groups? Do other reactions intervene such as hydrogen evolution or polymerization? Does the cleavage (eq. 16) of the dianion of 1,4-diphenylbutane occur?



(16)

Can less reactive substrates be cleaved by addition of 18-crown-6 or hexamethylphosporamide to the reaction mixture or increase of the reaction temperature?

(e) Cleavage of Carbon-Hydrogen Bonds by Cesium

Cesium is much more reactive than the other alkali metals in cleavage of carbon-hydrogen bonds but the mechanism of this reaction is unknown (see "Summary of Previous Work", Appendix I). Does the cleavage take place in a radical anion (as commonly supposed) or in a dianion? For cleavage of a radical anion , the mechanism recently given[40b] for reaction of cesium with alkylbenzenes is as follows as illustrated for toluene:

Mechanism IA

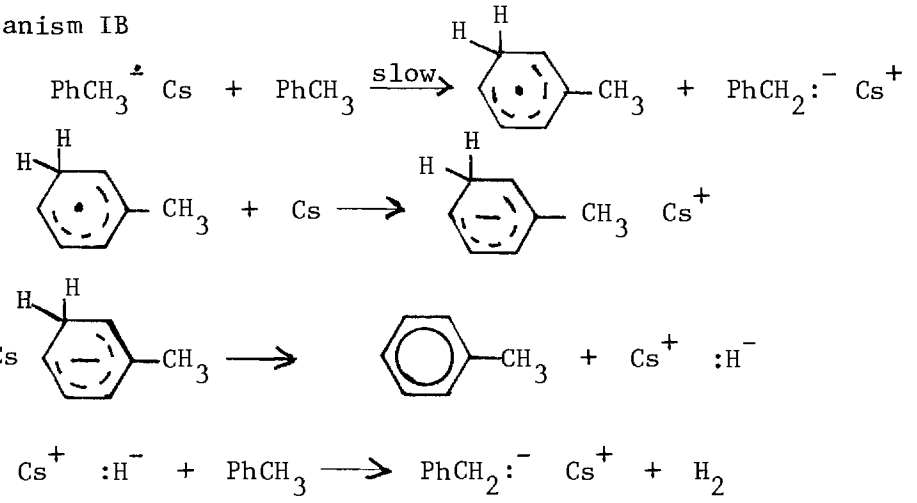
$$PhCH_3 + Cs \rightleftharpoons PhCH_3^{\dot{-}}\ Cs^+$$

$$PhCH_3^{\dot{-}}Cs \xrightarrow{slow} PhCH_2:^-\ Cs^+ + H\cdot$$

$$2H\cdot \xrightarrow{fast} H_2$$

This mechanism suffers from having a hydrogen atom as an intermediate and appears unlikely although it is widely quoted for metallation of radical anions[43c]. An alternative possibility as adapted from the mechanism of Eisch and Kaska[43a] for metalation of triphenylmethane by lithium biphenylide is given below:

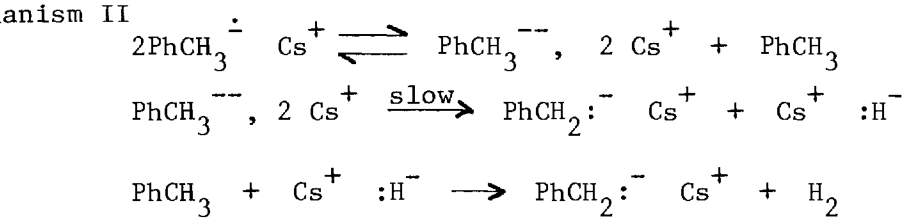
Mechanism IB



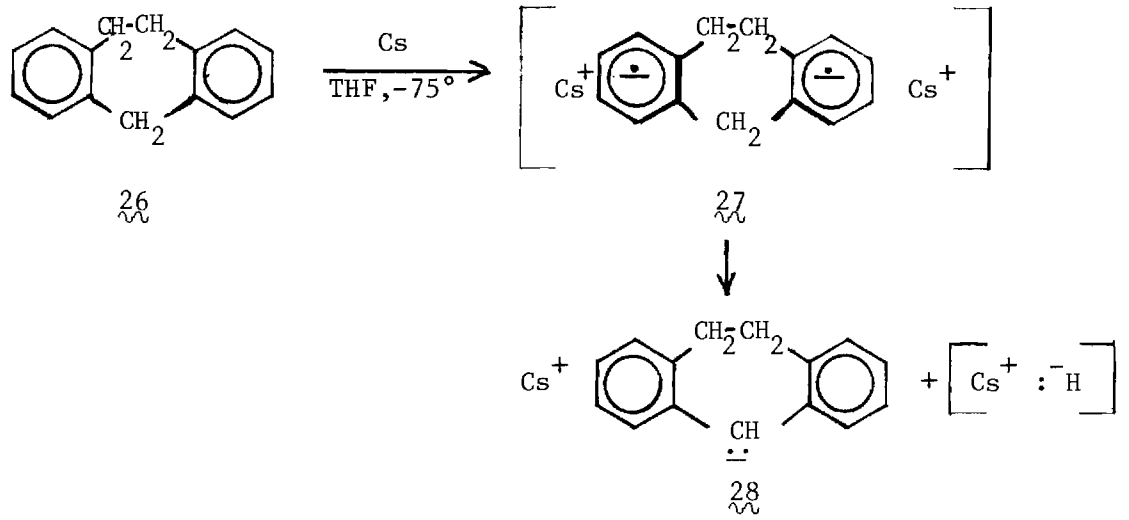
For this alternate mechanism it is surprising that Birch reduction products of toluene were not obtained instead of, or in addition to hydrogen since Eisch and Kaska[43a] obtained reduction products of biphenyl when metallating triphenylmethane with lithium biphenylide.

We wonder therefore, if the cleavage of carbon-hydrogen bonds by cesium does not occur in a dianion as given in Mechanism II.

Mechanism II



In agreement with this mechanism we have recently discovered that the hydrocarbon 26

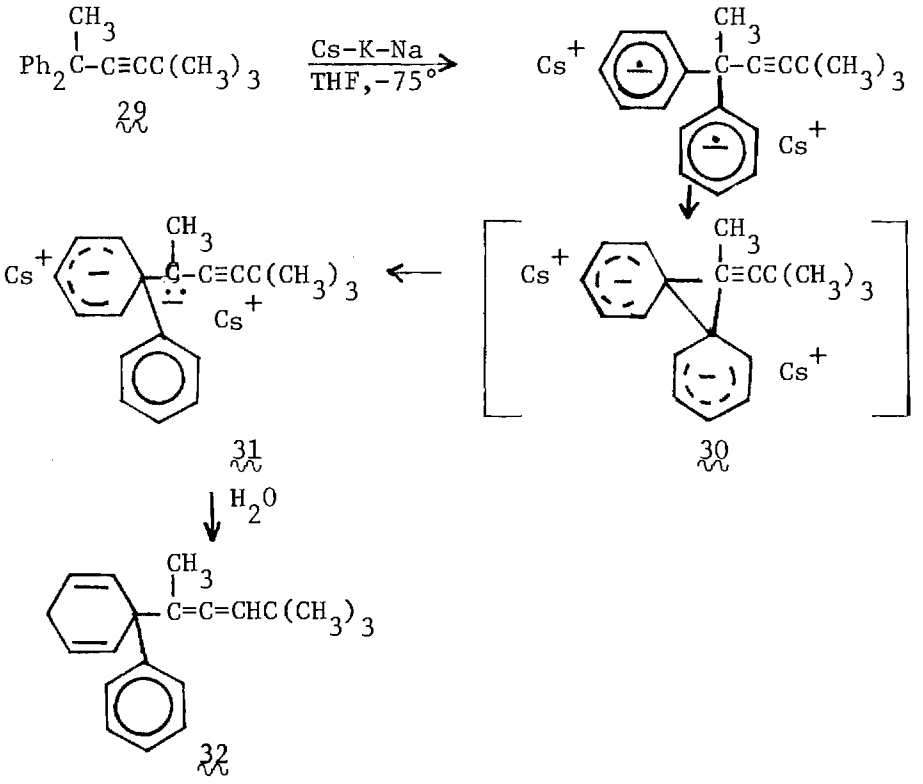


is quantitatively cleaved to 28 and is cleavaged some 45 times more readily than dibenzyl is cleaved to benzylcesium according to competitive experiments with dibenzyl. Since dibenzyl is cleaved as a dianion[61], it is tempting to speculate that the cleavage of 26 occurs by way of the dianion 27.

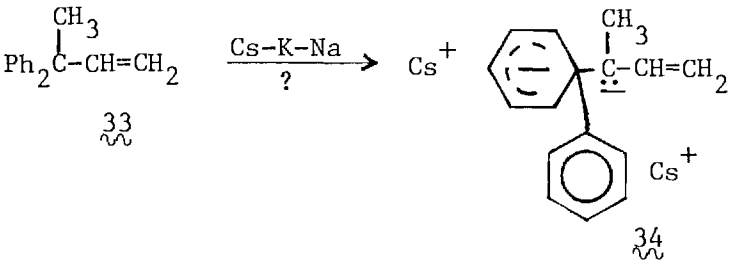
Mechanism IB differs from Mechanism IA and II in terms of its kinetic dependence on the concentration of hydrocarbon. Mechanism II differs from Mechanisms IA and IB in its kinetic dependence on the activity of cesium dissolved in the THF. In view of the known experimental difficulties[43c] of working with solutions of radical anions and especially of dianions, we propose studying the mechanism of metalation of 26, diphenylmethane, and fluorene by the technique of relative rate constants as determined by competition experiments with dibenzyl (or derivatives thereof) whose mechanism of cleavage by cesium has been established[61]. Constancy of relative rate constants under conditions of varying concentrations of reactant hydrocarbons and activity of cesium will be taken to indicate similarity of mechanism of C-H cleavage versus C-C cleavage. We propose to vary the activity of cesium by use of pure cesium metal, Cs-K-Na alloy, and Cs in THF complexed with 18-crown-6, benzene, and toluene. Whether cesium benzenide and toluenide will function as bases[43a] under the mild conditions of these metalation reactions and thus offer an alternate mechanistic pathway for metalation will be determined by looking for possible reaction products from these hydrocarbons upon carbonation of the reaction mixture.

(f) Skeletonal Rearrangements of Unsaturated Hydrocarbons by Cesium

We have recently discovered[62] that 5,5-dimethyl-2,2-diphenyl-3-hexyne (29) when reated with Cs-K-Na alloy in THF at -75° undergoes a remarkable rearrangement to 32 evidently by the scheme shown below.

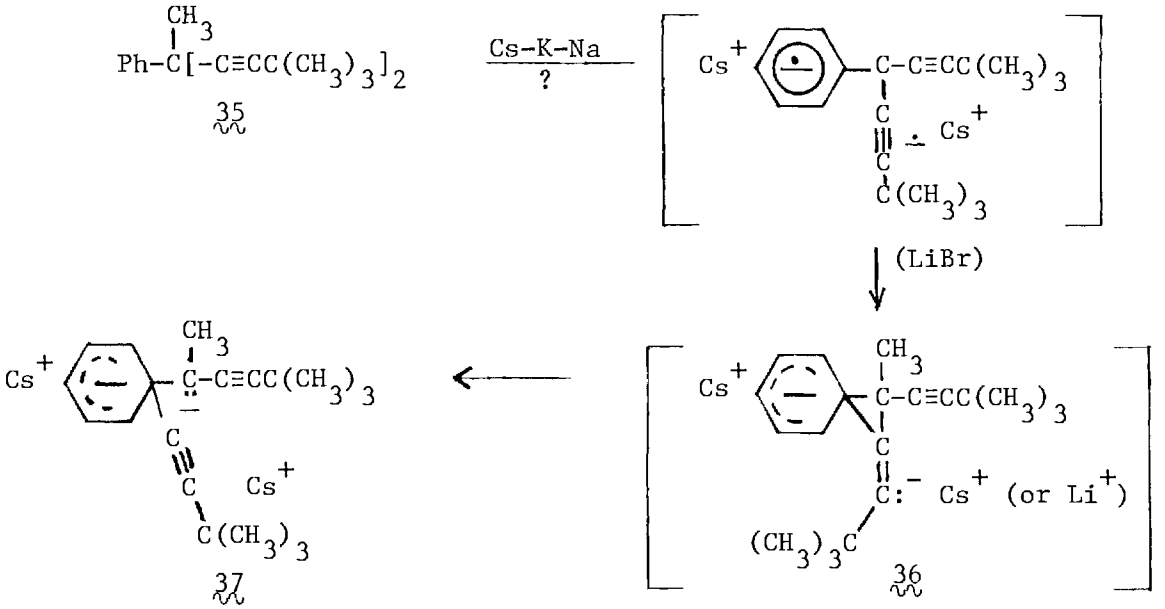


We wish to probe the generality of this rearrangement. Thus may the acetylene group be replaced by a vinyl group? Hence we plan to see if 3,3-diphenyl-1-butene (33) rearranges to 34 upon reaction with Cs-K-Na alloy in THF. This study will be undertaken

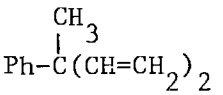


in conjunction with rearrangement of the related compound 7 (M = Cs, see Section 16).

Another question is can the migrating phenyl group in 29 be replaced by a group of very different structure. For simplicity and general interest we will try replacement of the phenyl group by an acetylene group and thus look for possible rearrangement of 2,2,5,8,8-pentamethyl-5-phenyl-3,6-nonadiyne (35) upon reaction with Cs-K-Na alloy. Our preconception is that the intermediate or transition state 36 will



not be favored with cesium as counter cation at the vinylic anion center of 36 (see 1a, "Alkynyl versus Phenyl Migration") but would be much more favorable with lithium. Hence if the rearrangement 35 to 37 is not observed with Cs-K-Na alloy in THF at -75°, then following reaction with the alloy we will add anhydrous lithium bromide to the reaction mixture to look for possible catalysis by lithium cation (or lithium metal, in the highly reducing medium). Should the reaction of 35 with Cs-K-Na alloy at -75° be complicated by cleavage of an acetylide group, or if time permits, this study will be repeated on the ethylenic analog, 3-methyl-3-phenyl-1,4-pentadiene (38).



There is an interesting report[63] that when toluene vapor is passed over sodium naphthalene at 90° it disproportionates to ethylbenzene and benzene while over sodium chrysene at 135° it gives o-xylene and benzene (but NO m- or p-xylene). We would like to confirm and extend these experiments since they seem to point to elements of organocesium chemistry which are unknown. In the most thoroughly studied related area Ichikawa and Tamaru[64] have made considerable progress in elucidating the mechanism of catalytic hydrogenation of olefins with molecular hydrogen over compounds of aromatic hydrocarbons with alkali metals For the dianion of tetracene they find that the dicesium complex hydrogenates ethylene 4700 fold faster than the dilithium or 2300 fold

faster than the disodium complex. Moreover they have deduced that hydrogen forms an ortho-dihydrogen addition compound with the aromatic hydrocarbon-alkali metal complex and that this addition compound serves to transfer a molecule of hydrogen to the olefin. Hence after confirming the reports for sodium we wish to examine cesium adducts of aromatic hydrocarbons for catalytic activity in the disproportionation of toluene. Do cesium adducts catalyze the disproportionation at considerably lower temperatures than reported for sodium adducts? Also which aromatic hydrocarbons give the most active catalysts and which the most selective catalysts for ethylbenzene versus o-xylene formation? Does the activity (selectivity) correlate with the electron affinity[63], the one-electron localization energy[65], or the ortho-bond-localization energy[64] of the aromatic hydrocarbon in the alkali metal adduct? Do the methyl and/or phenyl groups of toluene become attached to the catalyst? If the latter is true, various methyl or phenyl derivatives of the aromatic hydrocarbon may be isolable. Finally, does the catalytic activity of aromatic hydrocarbon-alkali metal adducts pertain only to films of the adducts on solid supports? Is the activity decreased by the presence of the vapors of ethers? Does catalytic activity extend to homogeneous solution in ethereal solvents?

BIOGRAPHICAL DATA FOR PRINCIPAL INVESTIGATOR

Name: Erling Grovenstein, Jr.

Rank: Professor, School of Chemistry

Education:

B.S. in Chemistry, Georgia School of Technology	1944
Ph.D. in Organic Chemistry, Massachusetts Institute of Technology	1948

Experience:

1.	Research Associate, Massachusetts Institute of Technoloy, Summer of	1948
2.	Assistant Professor of Chemistry, Georgia Institute of Technology	1948-49
3.	Associate Professor of Chemistry, Georgia Institute of Technology	1949-57
4.	Research participant, Oak Ridge National Laboratory, Summers of	1949,195
5.	Professor of Chemistry, Georgia Institute of Technology	1957-65
6.	Julius Brown Professor of Chemistry, Georgia Institute of Technology	1965-dat

Recent Publications:

(1) "Carbanions. XIV. 1,4-Migration of the p-Biphenylyl Group in Reactions of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Alkali Metals," E. Grovenstein, Jr., and J.-U. Rhee, J. Am. Chem. Soc., 97, 769 (1975).

(2) "Carbanions. XV. Tight and Loose Ion Pairs in Rearrangements of Organoalkali Compounds," E. Grovenstein, Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975).

(3) "Carbanions. XVI. Reactions of 4-Chloro-1-p-biphenylylbutane with Alkali Metals. Formlation of a Spiro Anion," E. Grovenstein, Jr., and S. Akabori, J. Am. Chem. Soc., 97, 4620 (1975).

(4) "Carbanions. 17. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," E. Grovenstein, Jr., and A. B. Cottingham, J. Am. Chem. Soc., 99, 1881 (1977).

(5) "Carbanions, 18. Spiro Anions from Reactions of 2- and 3-p-Biphenylylalkyl Chlorides with Cesium-Potassium-Sodium Alloy," J. A. Bertrand, E. Grovenstein, Jr., P-c. Lu, and D. VanDerveer, J. Am. Chem. Soc., 98, 7835 (1976).

(6) "Tricyclo[4.2.2.$0^{2,5}$]dec-9-ene-exo,endo 3,4:7,8-Tetracarboxylic Dianhydride," E. Grovenstein, Jr., D. V. Lao, and J. W. Taylor, Org. Photochem. Syn., 2, 97 (1976).

(7) Carbanions. 19. Reactions of Cesium or Cesium-Potassium-Sodium Alloy with Benzene and Toluene," E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).

(8) "Aryl Migrations in Organometallic Compounds of the Alkali Metals," E. Grovenstein, Jr., Adv. Organomet. Chem., 16, 167 (1977).

(9) "Phenyl Migration during Preparation of Grignard Reagents," E. Grovenstein, Jr., A. B. Cottingham, and L. T. Gelbaum, J. Org. Chem., 43, 3332 (1978).

(10) "Skeletal Rearrangements of Organoalkali Metal Compounds," E. Grovenstein, Jr., Angew. Chem., 90, 317 (1978); Angew. Chem. Int. Ed. Engl., 17, 313 (1978).

Personnel:

The project will be under the direction of Dr. Erling Grovenstein, Jr., Brown Professor of Chemistry at the Georgia Institute of Technology. Dr. Grovenstein plans to devote one fourth time during the academic year and half time during three summer months toward the proposed project. The budget requests support for the Principal Investigator only for the equivalent of full time work for 1.5 summer months. In addition support for one post-doctoral research associate and two graduate research assistants (preferably Ph.D. candidates) is requested as explained in the budget. The project should contribute to the training of students in chemistry.

First Year
beginning July 1, 1980

SUMMARY
PROPOSAL BUDGET

ORGANIZATION AND ADDRESS	FOR NSF USE ONLY
Georgia Institute of Technology Atlanta, Georgia 30332	PROPOSAL NO.
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR	DURATION (MONTHS) PROPOSED / REVISED
Erling Grovenstein, Jr.	12 /

NSF USE	A. SENIOR PERSONNEL (LIST BY NAME; SHOW NUMBERS OF PEOPLE IN BRACKETS; SALARY AMOUNTS MAY BE LISTED ON SEPARATE SCHEDULE) GPM 205.1b	NSF FUNDED MAN MONTHS CAL.	ACAD.	SUMR.	FUNDS REQUESTED BY PROPOSER	FUNDS GRANTED BY NSF (IF DIFFERENT)
	1. P.I./P.D. Erling Grovenstein, Jr.			1.5	$ 5,865	$
	2. CO P.I./P.D.				$	$
	3. CO P.I./P.D.				$	$
	4. CO P.I./P.D.				$	$
	5. CO P.I./P.D.				$	$
11115	6. ( ) ◄— SUBTOTALS A1 - A5 —►				$ 5,865	$
	FACULTY AND OTHER SENIOR ASSOCIATES (ATTACH EXTRA SHEET IF NECESSARY)					
	7.				$	$
	8.				$	$
	9.				$	$
	10.				$	$
	11.				$	$
11117	12. ( ) ◄— SUBTOTALS A7 - A11 —►				$	$
	B. OTHER PERSONNEL (LIST NUMBERS IN BRACKETS)					
11141	1. ( ) POSTDOCTORAL ASSOCIATES				$ 13,000	$
11149	2. ( ) OTHER PROFESSIONALS				$	$
11150	3. ( ) GRADUATE STUDENTS				$ 13,000	$
11152	4. ( ) UNDERGRADUATE STUDENTS				$	$
11182	5. ( ) SECRETARIAL - CLERICAL				$	$
11183	6. ( ) TECHNICAL, SHOP, OTHER				$	$
	TOTAL SALARIES AND WAGES (A+B)				$ 31,865	$
11200	C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) 10.51% of salary of PI				$ 616	$
	TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				$ 32,481	$
	D. EQUIPMENT (LIST ITEMS AND DOLLAR AMOUNTS FOR EACH ITEM) Minor miscellaneous items such as vacuum pumps, stirrers, etc.					
23181	TOTAL EQUIPMENT				$ 1,000	$
	E. MATERIALS AND SUPPLIES					
32630					$ 4,000	$
	F. DOMESTIC TRAVEL					
42111					$ 400	$
	G. FOREIGN TRAVEL (LIST DESTINATION AND AMOUNT FOR EACH TRIP; GPM 731) None					
42112					$	$

First Year beginning July 1, 1980

SUMMARY PROPOSAL BUDGET

PROPOSAL NO.

52500	H. PUBLICATION COSTS/PAGE CHARGES	$ 1,500	$
62315	I. COMPUTER (ADPE) SERVICES	$	$
	J. CONSULTANT SERVICES (IDENTIFY CONSULTANTS BY NAME AND AMOUNT; GPM 516)		
		$	$
	K. PARTICIPANT SUPPORT COSTS, IF ALLOWED BY PROGRAM GUIDE (ITEMIZE) GPM 518		
	1. STIPENDS $		
	2. TRAVEL $		
	3. SUBSISTENCE $		
	4. OTHER - SPECIFY $		
	5. TOTAL PARTICIPANT COSTS (K1 + K2 + K3 + K4)	$	$
	L. ALL OTHER DIRECT COSTS (List items and dollar amounts. Details of subcontracts, including work statements and budget, should be explained in full in proposal.)		
	$		
	$		
	$		
	$		
65001	TOTAL OTHER DIRECT COSTS	$ 39,381	$
	M. TOTAL DIRECT COSTS (A THROUGH L)	$	$
	N. INDIRECT COSTS (Specify rate(s) and base(s) for on/off campus activity. Where both are involved, identify itemized costs included in on/off campus bases in remarks.) 73.0% of Salaries and Wages on Campus		
74100	TOTAL INDIRECT COSTS	$ 23,261	$
	O. TOTAL DIRECT AND INDIRECT COSTS (M + N)	$ 62,642	$
74500	P. LESS RESIDUAL FUNDS (If for further support of current project; GPM 252 and 253)	$	$
75000	Q. AMOUNT OF THIS REQUEST (O MINUS P)	$ 62,642	$

REMARKS

Georgia Institute of Technology will cost share in accordance with current Foundation policy.

NOTE: SIGNATURES REQUIRED ONLY FOR REVISED BUDGET (GPM 233). THIS IS REVISION NO.

SIGNATURE OF PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR	DATE OF SIGNATURE	TYPED OR PRINTED NAME AND TITLE
SIGNATURE OF AUTHORIZED ORGANIZATIONAL REPRESENTATIVE	DATE OF SIGNATURE	TYPED OR PRINTED NAME AND TITLE

FOR NSF USE ONLY

INDIRECT COST RATE VERIFICATION			PROGRAM OFFICER APPROVAL
Date Checked	Date of Rate Sheet	Signature	

Grant Number	Amend No.	Institution	Organization	Fund Acct.	Program	Object

	Proposal Number	Dur.	Chg.	Award Date	Proposed Amount	Prpsd. Dur.	

Budget Summary, Four Year Period

The detailed budget for the first year of the grant as given on the preceeding two pages totals $62,642. The budget estimated for the 2nd, 3rd, and 4th years with a 7% increase per year to cover inflation is $67,027, $71,719, and $76,739 respectively for a total of $278,127 for the four year period.

Current and Pending Support

Current Support

Current outside support for the Principal Investigator, Erling Grovenstein, Jr., is restricted to National Science Foundation Grant No. CHE-7602720, entitled "Chemistry of Carbanions" which expires June 30, 1980. The Principal Investigator devotes one fourth time during the academic year and half time during the summer toward this research.

Pending Support; Other Agencies

There are no pending proposals and no support from other agencies for the research outlined in this proposal will be sought while the proposal is under consideration by the National Science Foundation.

Total Expenditures and Commitment under Existing NSF Grant CHE-7602720 to Date at which New Funding is Desired (July 1, 1980).

Expenditures through November 30, 1979

Personal Services	$ 74,717.03
Fringe Benefits	1,506.10
Expendable supplies and materials*	15,406.30
Equipment	25.00
Domestic Travel	316.70
Total Direct Costs	$ 91,971.13
Indirect Costs	53,348.95
Total Expenditures through Nov. 30, 1980	$145,320.08

Anticipated Additional Expenditures Jan. 1, 1979 - Oct. 31, 1979:

Expendable supplies and materials*	$ 679.92
Total Direct Costs	$ 679.92
Indirect Costs	none
Total Anticipated Expenditures Dec. 1, 1979 - June 30, 1980	$ 679.92
Total Expenditures through Nov. 30, 1980	145,320.08
Total Projected Expenditures	$146,000.00
Amount of this Grant	$146,000.00
Projected Residual Balance	none

*This item includes publication costs and analyses.

APPENDIX I

SUMMARY OF PREVIOUS WORK

The following brief summary of examples which are known to the chief investigator should make it clear that the organometallic chemistry of lithium and cesium is markedly and usefully different.

1. Reaction of Alkali Metals with Carbon

Lithium and sodium when heated with carbon form the acetylides Li_2C_2 and Na_2C_2. The heavier alkali metals including cesium react with carbon but give non-stoichiometric interstitial compounds where the metal atoms enter between the planes of carbon atoms in the lamellar graphite structure[4].

2. Metalation of Hydrocarbons by Alkali Metal Alkoxides

The metalation of hydrocarbons by alkali metal alkoxides[9,10] in tetrahydrofuran

$$Ph_3CH + MOC(CH_3)_3 \rightleftharpoons Ph_3C{:}^-M^+ + HOC(CH_3)_3 \quad (1)$$

is an equilibrium process whose equilibrium constant increases with the alkali metal M along the series Li < Na < K < Cs. While exact values of the equilibrium constant are not known, the differences are quite large between lithium t-butoxide and cesium t-butoxide.

3. Metalation of Hydrocarbons by Alkali Metal Amides

Equilibrium in reaction of diphenylmethane in liquid ammonia with alkali metals amides[10]

$$Ph_2CH_2 + MNH_2 \rightleftharpoons Ph_2CH{:}^-M^+ + NH_3 \quad (2)$$

is such that while diphenylmethylsodium,-potassium, and, doubtlessly, -cesium are stable in liquid ammonia, diphenylmethyllithium undergoes essentially complete ammonolysis to diphenylmethane and lithium amide. In diethyl ether solution, potassium amide will metalate diphenylmethane but sodium amide is unable to metallate this hydrocarbon. Thus the order of metalating ability of the alkali metal amides appears to be: Li < Na < K(< Cs).

In cyclohexylamine, Streitwieser[11] and coworkers found diphenylmethane to be completely converted to its anion by cesium cyclohexylamide but incompletely converted by lithium cyclohexylamide. Thus the equilibrium basicity of cesium cyclohexylamide is greater than that of lithium cyclohexylamide. With respect to its kinetic basicity toward ionization of hydrocarbons, cesium cyclohexylamide is up to 35,000 times more reactive than lithium cyclohexylamide in cyclohexylamine as solvent[11].

4. Isotopic Exchange Between D_2 and Cyclohexylamide Salts

Deuterium isotope exchange between molecular hydrogen and cyclohexylamine is catalyzed by cyclohexylamide alkali metal salts (MCHA) with the observed order being CsCHA $\gtrsim$ KCHA > NaCHA >> LiCHA. The cesium salt is at least 10^3 times more reactive than the lithium salt[12]. It was thought likely that the transition state in the exchange was stabilized by a cation with the extent of stabilization dependent on the size and polarizability of the particular cation M^+ and the type of cyclohexylamide alkali metal ion pair involved.

5. Reaction of Phenylethynylalkali Compounds with Benzonitrile

In an early semi-quantitative study Gilman and Young[13] found that the relative rate of addition of suspensions of phenylethynylalkali compounds, $C_6H_5C{\equiv}CM$, to benzonitrile in diethyl ether followed the order of increasing reactivity: RLi << RNa < RK < Rb < RCs.

6. Metal-Metal Exchange of Organolithium Compounds with Alkali Metal Alkoxides

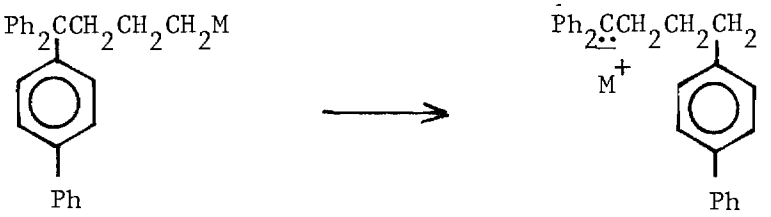
Organosodium and potassium compounds may be formed by the reaction of sodium and potassium alkoxides with organolithium compounds in hydrocarbon solvents[14].

$$RLi + MOR' \longrightarrow RM + LiOR' \qquad (3)$$

The conversion of organolithium compounds to organosodium, -potassium, and-cesium compounds by sodium, potassium and cesium t-butoxide respectively in tetrahydrofuran solution is evidently the basis for catalysis of the rearrangement of organolithium compounds by alkali metal alkoxides[15-17]. That equilibrium (3) lies far to the right with the heavier alkali metals is evidently due to the much stronger bonding of lithium to oxygen as opposed to carbon, and the comparative more near equivalence in bonding of the heavier alkali metals to oxygen versus carbon.

7. Relative Rates of Rearrangement of Organoalkali Metal Compounds

In ethereal solvents the relative rate of [1,4] migration of p-biphenylyl (eq.4)



(4)

in 4-p-biphenylyl-4,4-diphenylbutylalkali metal compounds versus the rate of protonation of the organoalkali compound by solvent increases[15] along the series: Li << Na << K or Cs. While the absolute rates have not been measured, the differences in relative rate appear to be large. The same relative ease of rearrangement with variation of alkali metal appears to hold for other rearrangements of organoalkali metal compounds[18,19]; the differences in rate are such that while an organolithium compound is found to be negligibly rearranged after hours at -75°, the corresponding organocesium compound is completely rearranged within one minute or less at the same temperature in the same solvent.

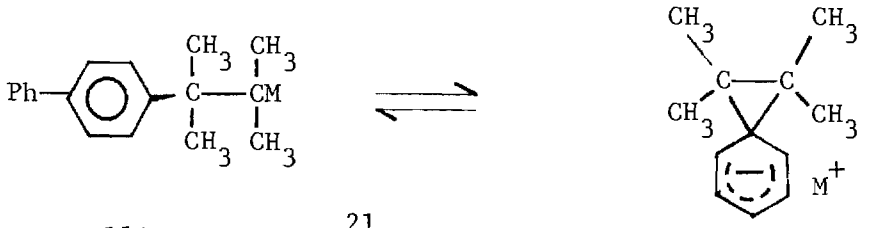
8. Ring-Chain Tautomerism of Unsaturated Organoalkali Metal Compounds

Maercker and Roberts[20] have reported that 4,4-diphenyl-3-butenylalkali compounds undergo reversible cyclization as shown in eq. 5. For M = Li in diethyl

(5)

ether as solvent only the open form of the organometallic is observable at equilibrium while with M = Na or K only the cyclic (cyclopropyl) compound is detectable. In tetrahydrofuran as solvent only the cyclic compound is detectable with any of these counter cations.

Similarly in the system of eq. 6 with 2-p-biphenyl-1,1,2-trimethylpropyl anion in tetrahydrofuran, lithium as counter ion gives only the open form of the organometallic while with cesium a four to one mixture of the spiro to the open form

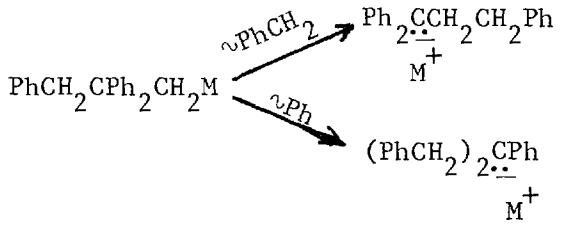


(6)

of the organometallic is present[21].

9. Variation of Migratory Aptitudes of Groups in Organoalkali Rearrangements with Alkali Metal Cation

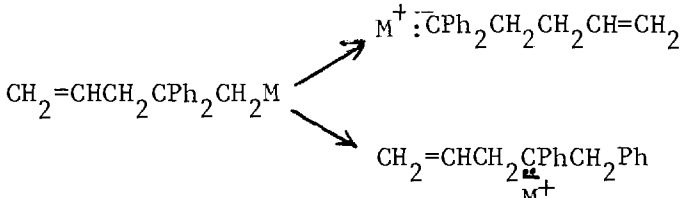
2,2,3-Triphenylpropylalkali compounds may undergo [1,2] migration of either the benzyl or phenyl groups (see eq. 7).



(7)

With lithium and sodium as counter cation in tetrahydrofuran only migration of benzyl was observed whereas with potassium appreciable phenyl migration and with cesium predominant phenyl migration was observed[16]. The effect of solvent, temperature, and added ligands (18-crown-6) on the migratory aptitudes led to the conclusion that benzyl migration occurred in a loose ion pair by elimination and re-addition of benzyl anion to intermediate 1,1-diphenylethene whereas phenyl migration occurred in a tight ion pair by an intramolecular process.

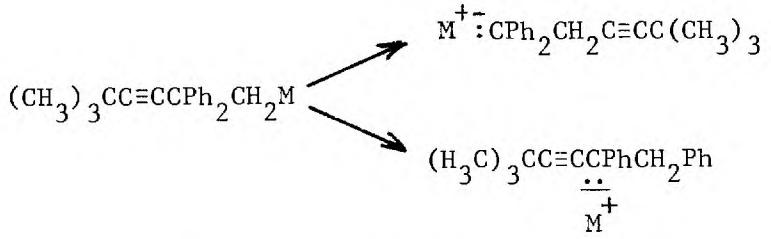
In the related rearrangement of 2,2-diphenyl-4-pentenyl alkali metal compounds[17], lithium as cation gave chiefly migration of the allyl group whereas with potassium the product consisted of 68% or with cesium 84% of the product of phenyl migration (eq.8).



(8)

Again the effect of solvent, 18-crown-6, temperature, cation, and other evidence was to suggest that allyl migration occurred in a highly solvated transition state (or loose ion pair) while phenyl migration occurred in a less solvated transition state or tight ion pair.

In the above two examples, benzyl migration always and allyl migration for certain under some conditions (or possibly under all) occur by a cleavage recombination mechanism and hence by a very different mechanism from that of phenyl migration. We have recently discovered a case in which the migration of two groups, phenyl and acetylene, occurs with a large cation effect upon migratory aptitudes and yet both migrations occur evidently by a similar intramolecular mechanism. Thus in the rearrangement of 5,5-dimethyl-2,2-diphenyl-3-hexynylalkali compounds (eq. 9), with lithium as cation only [1,2] migration of the acetylene group

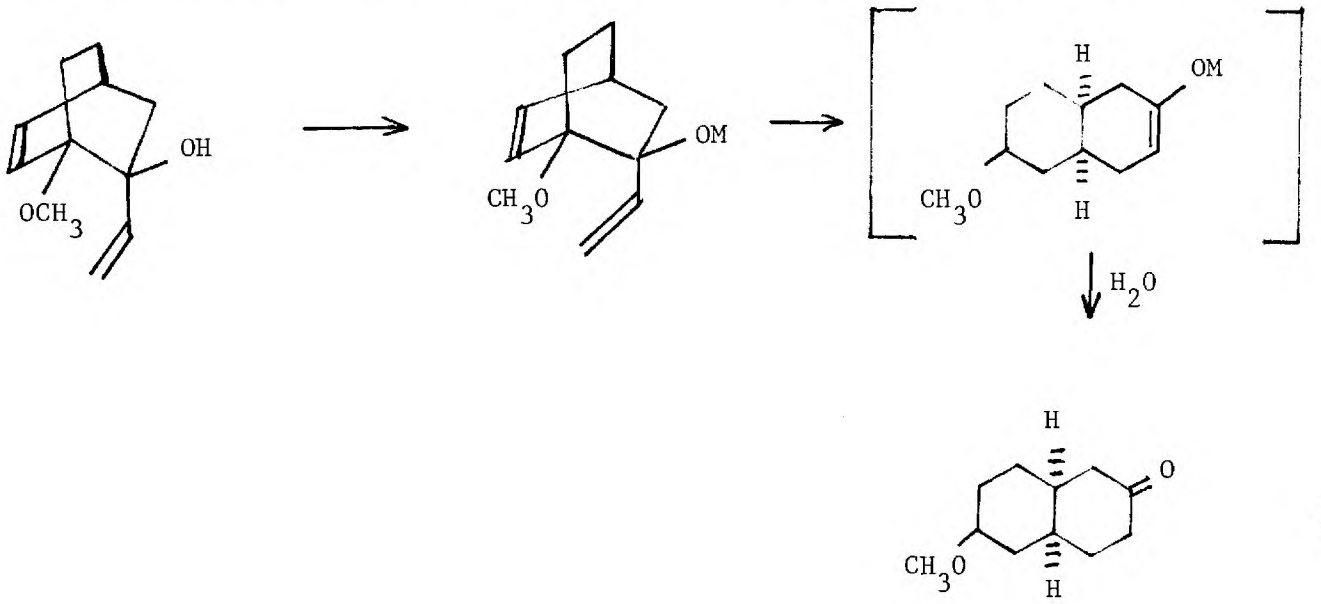


(9)

occurs while with cesium only [1,2] migration of phenyl occurs in the initial process[22].

10. Cation Effects upon the Rate of [3,3] and [1,3] Sigmatropic Rearrangements

In detailed studies upon the oxy-Cope rearrangement Evans and Golob[23] found that 1,5-hexadiene alkoxides rearranged much more readily than the corresponding alcohol and that the rate of rearrangement was both cation and solvent (or ligand) dependent (see eq. 10). Thus when M was Li after 24 hr at reflux in tetrahydrofuran



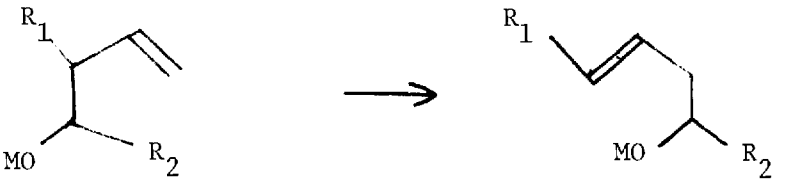
(10)

(66°) there was no evidence for rearrangement; whereas when M was Na under similar conditions the half-life for rearrangement was 72 min; when M was K, the half-life was 1.4 min. When M was potassium complexed with 18-crown-6 at 0° in THF the rearrangement was accelerated 180 fold over potassium in absence of crown. The potassium derivative complexed with 18-crown-6 underwent rearrangement 10^{12} times faster than the alcohol; for a related system (see eq.10, CH_3O replaced by H) the acceleration was 10^{17} fold.

Steigerwald, Goddard, and Evans[24], employing ab initio generalized valence bond and configuration interaction methods, have calculated C-H bond energies (see eq. 11) for CH_3OH, CH_3ONa, CH_3OK, and CH_3O^- of 90.7 (cf experimental value of

$$CH_3OM \longrightarrow \cdot CH_2OM + H\cdot \qquad (11)$$

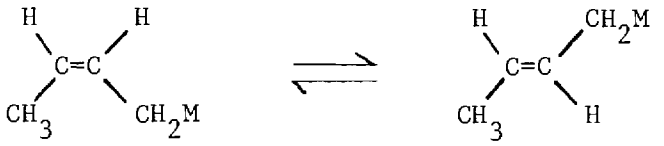
91.8 ± 1.2), 80.6, 79.0, and 74.2 kcal/mole, respectively. These authors suggest that similar oxy substituent effects help explain the marked rate enhancements in the above oxy-Cope rearrangement and in related [1,3] sigmatropic rearrangements[25] (see eq.12).



(12)

11. Cation Effects upon the Stereochemistry of Allylic Anions

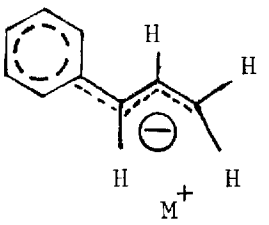
Schlosser and Hartmann[26] have reported that the equilibrium Z/E isomeric composition of various 2-alkenylmetallic compounds is dependent upon the metal. Thus for the 2-butenyl system (see eq.13) the % Z isomer (rest E isomer) increases



(13)

as M = H, MgBr, Li, Na, K, and Cs, the % Z isomer in hexane being 23, 54, 67, 93, 94, and 99.9 respectively. It was suggested that the predominant formation of the Z isomer with Cs^+ as counter cation reflects the superior stability of the Z-butenyl anion, possibly because of hydrogen bonding between the terminal methyl group and the cis-anionic center[26]. The extent of hydrogen bonding evidently decreases with increasing carbon to M bonding[27].

The rotational barriers about the partial double bonds in allylic alkali metal compounds are dependent upon the alkali metal used. Thus for the phenylallyl metallic compounds[28] in tetrahydrofuran solution the temperature at which the ^1H NMR

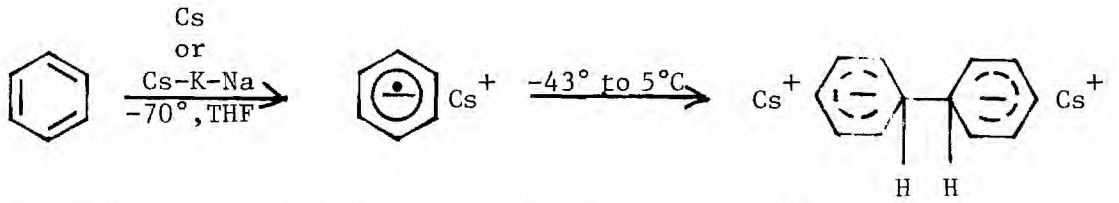


methylene signals coalesced was about 60°, 95°, and 115° for M = Li^+, Na^+, and K^+ respectively. Schlosser and coworkers[26] have found that simple allylpotassium derivatives undergo Z/E configurational changes very slowly compared to the corresponding allyllithium derivatives. Traces of oxygen, however, trigger Z/E isomerization of alkenylpotassium compounds[29]. For the uncatalyzed isomerization it is generally believed that bonding of the alkali metal cation to one end of the allylic anion in the transition state reduces the rotational barrier appreciably. It has been suggested that larger and more electropositive alkali metals do not stabilize the more localized transition state as well as the delocalized ground state whereas smaller metals, especially lithium, because of greater covalent character in the metal to carbon bonding are relatively better at stabilizing the localized transition state. It is stated that preliminary quantum mechanical calculations[30] on allylsodium versus allyllithium confirm this conclusion but these calculations seem not yet to have appeared. A similar explanation likely applies to many of the cation effects summarized above.

12. Superior Reducing Power of Metallic Cesium over Other Alkali Metals

We have noted above that the ionization energy of cesium in the vapor phase in considerably smaller than that of lithium. That this property also extends to ethereal solvents is denoted by the solubility of cesium[31] in tetrahydrofuran (as evidenced by the moderately deep blue solution at -75°) which far exceeds the solubility of potassium (which gives such a pale blue solution that the color is not easily detectable), which in turn exceeds that of sodium or lithium which are not visibly soluble even in the better solvent 1,2-dimethoxyethane[32].

Chemical evidence for the superior reducing power of metallic cesium over the other alkali metals in ethereal solvents is given by the reaction[33] of cesium in tetrahydrofuran with benzene to give cesium benzenide at -70°C and derived products (via the dimer) at higher temperature in yields which are nearly quantitative (see eq.14).



(14)

In contrast with Na-K alloy at -83°C in 2:1 by volume of THF to 1,2-dimethoxyethane, benzene is converted at equilibrium to radical anion[34] only to about 0.1%. In agreement we have observed[33] that with Cs-K-Na alloy in THF the product is exclusively the cesium derivative, not detectably the sodium or potassium derivative.

Another indication of the superior reducing power of cesium in contrast to the other alkali metals is provided by the reduction of ethylene with hydrogen over cesium as catalyst[35] at temperatures of 20 to 200°. Rubidium showed only weak

$$CH_2{=}CH_2 + H_2 \xrightarrow{Cs} CH_3CH_3$$

catalytic activity while potassium and sodium were inactive catalysts under these conditions. Hackspill and Rohmer[36] found that ethylene combines with cesium at 25 to 45° to give a brown substance which they claim (without detailed evidence) has the composition $C_2H_4Cs_2$; the brown product upon reaction with water vapor gives ethane. Clusius and Mollett[37] qualitatively confirmed these observations but noted that ethane and butane (or isobutane) were also produced (even in absence of added elemental hydrogen or protic solvents) and that the solid residue after addition of water yielded hydrogen, ethane, carbon, and unsaturated higher hydrocarbons (with excess of ethylene, the olefins C_6H_{12}, C_8H_{16}, and $C_{10}H_{20}$ of unknown structure were reported in good yield). In contrast rubidium[37] showed essentially no reaction with ethylene (97% recovery of ethylene after 3 years reaction time). While the cesium-catalyzed hydrogenation of ethylene is of unestablished mechanism, it appears likely that it is the cesium adduct of ethylene which reacts with hydrogen to give, perhaps in several steps, ethane[38].

Finally cesium reacts with toluene at 28.5°C to give benzylcesium with evolution of hydrogen[39]. Analogous reactions of cesium occur with m-xylene, mesitylene, isopropylbenzene, etc, but similar reactions of the other alkali metals are unknown unless two or three aryl groups are present on one carbon atom to provide activation. Thus potassium reacts with triphenylmethane in 1,2-dimethoxyethane to give triphenylmethylpotassium[41] but hydrogen is not evolved, instead cleavage and reduction products are formed. Also diphenylmethane reacts with potassium to give diphenylmethylpotassium[42]. While the mechanism of these metalations is not

known with certainty, it is generally agreed that the first step involves formation of a radical anion[43]. In the reaction of alkali metals with fluorene in THF to produce fluorenyl anion[44], potassium radical anion had a free energy of activation 6.0 kcal/mole less than lithium (or 25,000 fold greater reactivity at 25°C) while cesium radical anion was described as decomposing too fast to measure even at -60°C. Although the reactivity of alkali metals with hydrocarbons parallels the gas-phase reducing power of the alkali metal, some property of the alkali metal other than reducing power may be responsible for the relative reactivity in metalation of fluorene. It has been suggested that the role of the cation consists in localization of the negative charge near the carbon atom of the C-H aliphatic bond which is to be broken[44]; evidently the heavier the alkali metal, the less its cation is solvated and the closer the cation can approach the site of the C-H bond. Also at the same distance of approach, a heavy alkali metal is expected to be more effective in transferring charge than a light alkali metal because of its greater polarizability. In this regard an electron spin resonance study of potassium, rubidium, and cesium benzenide solutions shows that the metal hyperfine splitting increases for the alkali metal cations from potassium to cesium and theoretical calculations suggest that for a fixed distance between the metal ion and the plane of the benzene ring, the amount of unpaired charge density on the metal increases from potassium to cesium[45]. It should be noted, however, that since the mechanism of these metalation reactions is not firmly established, any detailed interpretation remains in some doubt.

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APPENDIX II

Summary of Progress to Date upon "Chemistry of Carbanions"

NSF Grant CHE 76-02720 For Period Jan. 1, 1976 - Dec. 31, 1979

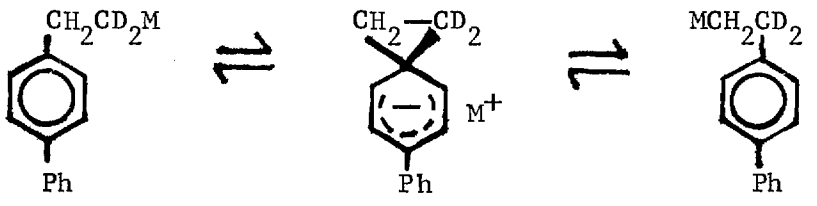
by Erling Grovenstein, Jr., Principal Investigator

PART I. Studies upon Rearrangements of Carbanions

The simplest reaction which a carbanion (i.e., an organoalkali metal compound) can undergo would appear to be a molecular rearrangement. Since knowledge about the occurrence or non-occurrence of such a reaction would appear necessary for successful procedures using carbanion as synthetic reagents and because carbanions are the most useful of the three possible trivalent forms of carbon in organic syntheses, expecially for formation of new carbon-carbon bonds, much of our effort has been directed toward learning the structural features and reaction conditions necessary for rearrangements of carbanions.

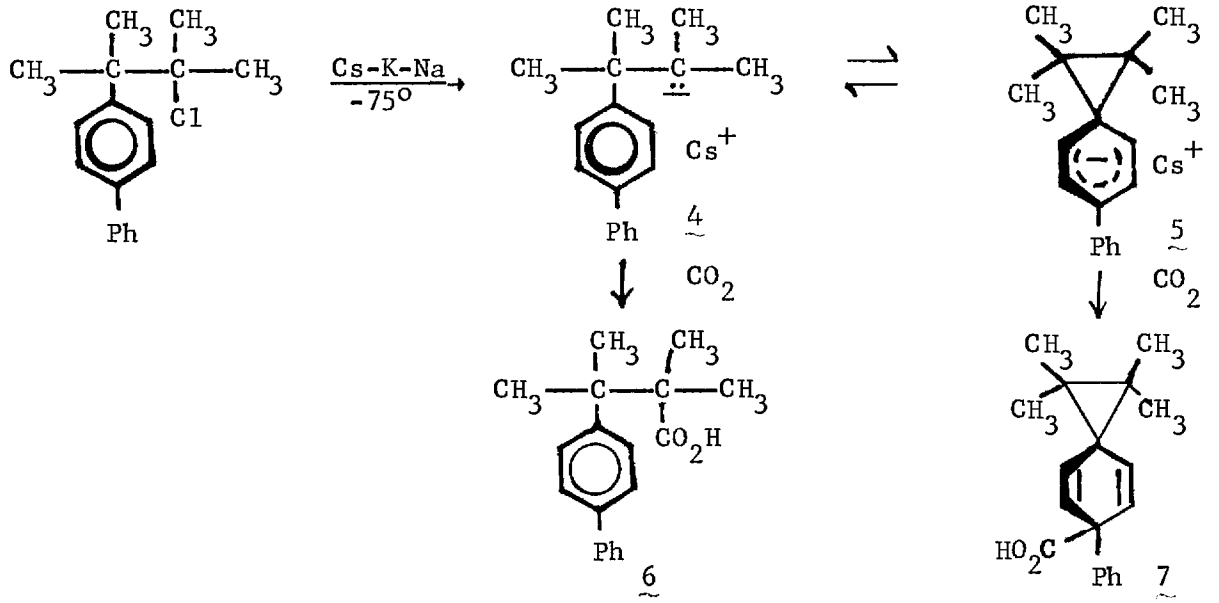
A. [1,2] Migration of p-Biphenylyl in 2-p-Biphenylylethyl Anions and Radicals

Spiro anions have long been suggested as intermediates or transition states in migrations of aryl groups in organoalkali compounds. While 2-p-biphenylylethylpotassium and -cesium undergo ready rearrangement[1] (1 → 3) in tetrahydrofuran (THF), attempts to detect the intermediate spiro anion 2 in the reaction of 2-chloro-1-p-biphenylylethane with excess



1 2 3

Cs-K-Na alloy in THF at -75° for one minute before carbonation indicated less than 1% (if any) of the desired spiro anion in the reaction mixture even though most of the starting chloride had been consumed. In contrast reaction of 2-p-biphenylyl-3-chloro-2,3-dimethylbutane with Cs-K-Na alloy in THF at -75°C for one minute gave after carbonation some 28% of the spiro acid 7 and 7% of 3-p-biphenylyl-2,3,3,-trimethylbutanoic acid 6 as shown in the scheme below. This work has been published in a preliminary communication[2] which includes



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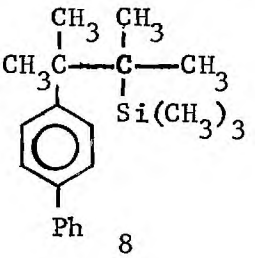
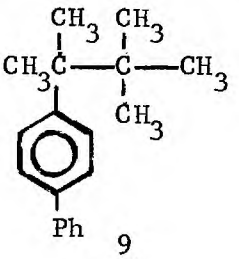
lso an x-ray diffraction study to confirm the structure of 7.

In unpublished work the mobile equilibrium between 4 and 5 has been established by everal techniques. First the half-life of the spiro anion 5 and of the open anion 4 re each about 22 minutes in THF at -75°C as determined from the results of carbonation. his finding is surprising for anions of such dissimilar structure as 4 and 5 but can e readily understood if 4 and 5 are in mobile equilibrium. Second the mixture of rganocesium compounds 4 and 5 when allowed to react with trimethylsilyl chloride or imethyl sulfate gives only the open derivatives 8 and 9 respectively and no spiro

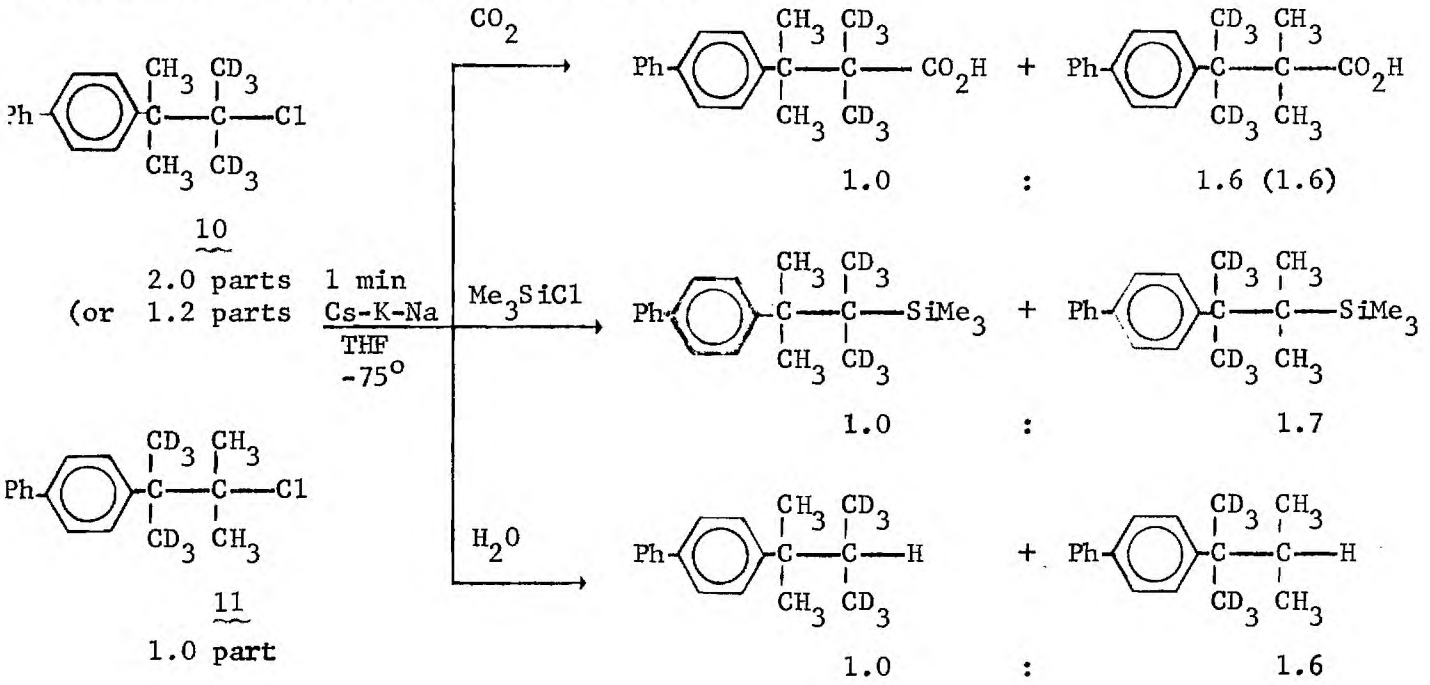


8



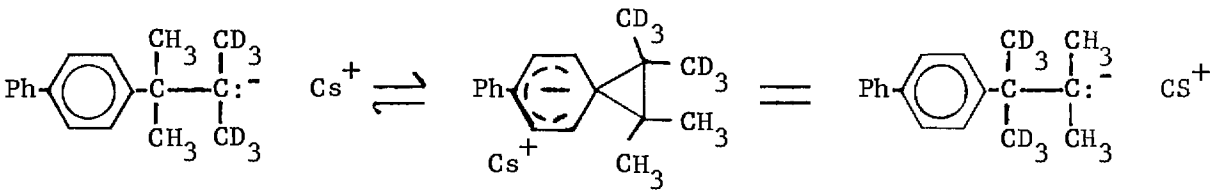
9

roducts. These results are understandable on the basis that, for a mobile equilibrium (4) ⇌ (5), certain reagents may attack one of the isomeric anions more readily than the ther. In particular the less reactive dimethyl sulfate and trimethylsilyl chloride likely react preferentially with the localized anion 4 rather than with the delocalized nion 5 while the more reactive carbon dioxide reacts unselectively with both 4 and 5. inally confirmation comes from studies with the 2.0 to 1.0 mixture of the deuterium abeled chlorides 10 and 11 respectively which gave the product ratios with various lectrophiles as shown in the scheme below:



Note that even when the ratio of 10 to 11 was 1.2 to 1.0 the product ratio on carbonation was identical to that starting with the usual 2.0 to 1.0 ratio of 10 to 11. In summary

The experiments with the deuterium-labeled chloride confirm that cesium alloy reacts with the chloride to give the spiro anion 12 which is in mobile equilibrium with the open anions 13 and 14. If the results of carbonation can be relied upon to measure the position of equilibrium, the equilibrium may be depicted as shown below:

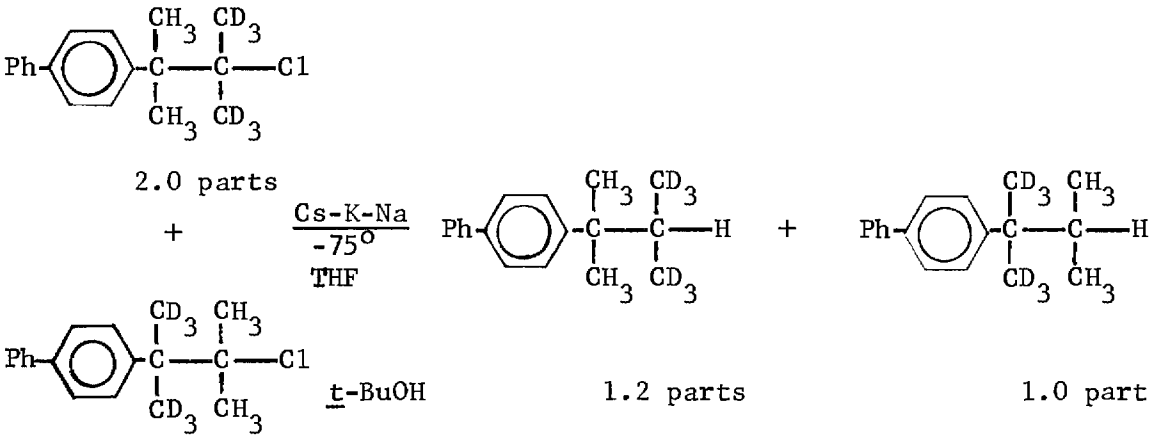


13 12 14

1.0 part 9 parts 1.6 parts

The ratio of 14 : 13 of 1.6 : 1.0 reflects a large secondary deuterium isotope effect and is of the correct magnitude expected for such an effect by analogy to that quoted[3] for $(CD_3)_3N$ in equilibrium with $(CH_3)_3N^+H$ in the gas phase and may be explained in terms of a recent theory[4] of anionic hyperconjugation involving the methyl groups.

The question arises does the rearrangement outlined above in terms of the anions 13 ⇌ 12 ⇌ 14 in fact occur in intermediate free radicals rather than carbanions. We answer this question in the negative on the basis, in part, that it is possible to "trap" the reactive intermediate prior to rearrangement by carrying out the reaction with Cs-K-Na alloy in THF in presence of small amounts of alcohols as shown below. Note that as



2.0 parts + Cs-K-Na, -75°, THF

1.0 part	t-BuOH	1.2 parts	1.0 part
1.0 part	CH_3OH	1.45 parts	1.0 part

The acidity of the alcohol decreases from methanol to tert-butyl alcohol the amount of rearrangement decreases. The alcohols should be good "traps" for carbanions but should be less effective in donating hydrogen atoms to free radicals than the solvent tetrahydrofuran[5]. Hence the formation of carbanions from our alkyl chloride precedes the rearrangement step itself.

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[3] J. F. Wolf, J. L. Delvin, P. J. DeFrees, R. W. Taft, and W. F. Hehre, J. Am. Chem. Soc., 98, 5097 (1976).

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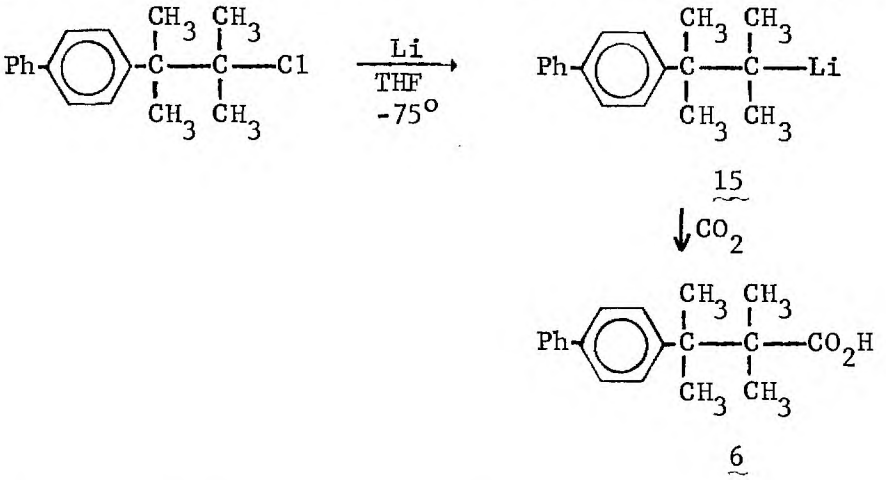
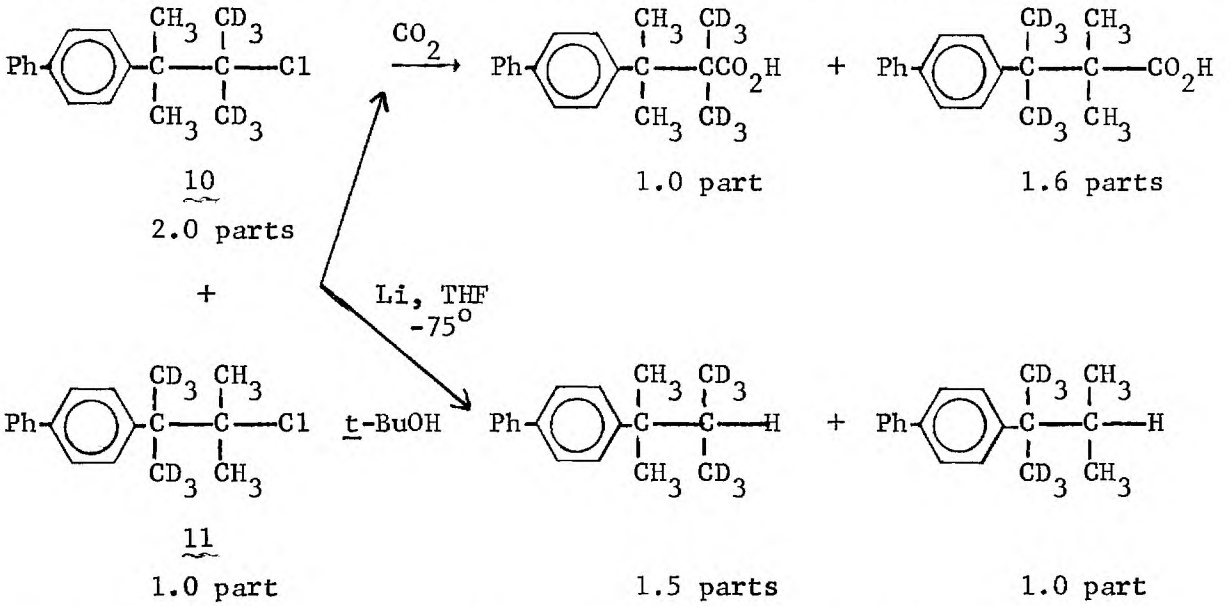
[5] Cf. W. A. Pryor, Chem. and Eng. News, June 7, 34 (1971).

Reaction of 2-p-biphenylyl-3-chloro-2,3-dimethylbutane in THF with lithium metal gives only the open lithium compound 15 with no evidence for appreciable spiro anion as shown by carbonation experiments which give only the acid 6. When, however, the

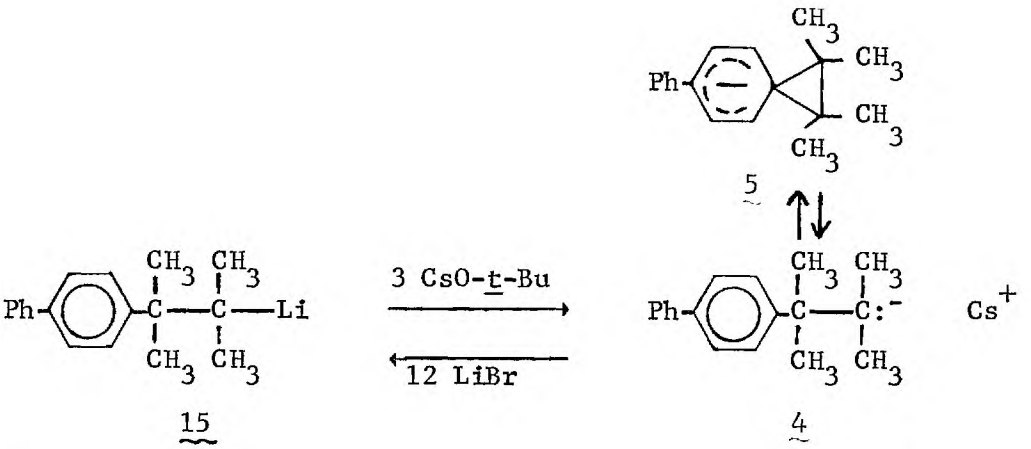


deuterium labeled chloride 10-11 is employed the open acid 6 has the same deuterium distribution as in reaction of the chloride with Cs-K-Na alloy. Obviously the



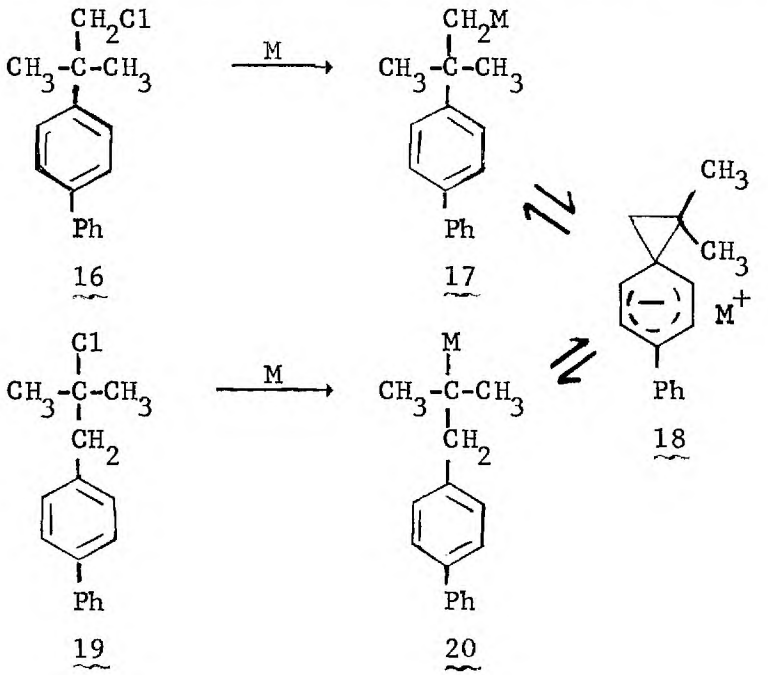
organolithium compound 15 is undergoing ready [1,2] migration of the p-biphenylyl group. That it is the carbanion (or organolithium compound) which is rearranging rather than a free radical is shown above by "trapping" experiments with tert-butyl alcohol. Again carbanions are "trapped" by the alcohol prior to appreciable rearrangement.

The open organolithium compound 15 serves as a convenient source of the open organocesium compound 4 which is formed by metathesis of 15 with CsO-t-Bu in THF at -75°. Since the open cesium anion 4 is in mobile equilibrium with the spiro anion 5, cesium tert-butoxide serves as a convenient reagent to bring about spiro cyclization at low temperature. Also the equilibrium mixture of 4 and 5 may be converted into the



pen organolithium compound 15 by metathesis with LiBr in THF at -75°. These eversible changes (which are established by examination of the products of carbonation), e believe, provide further and convincing evidence that the spirocyclization and [1,2] igration of p-biphenylyl is occurring in a carbanion or organoalkali compound rather han in a free radical.[6] Cation effects similar to those reported here were obtained y Maercker and Roberts[6] in their study of the cyclopropylcarbinyl-homoallyl earrangement.

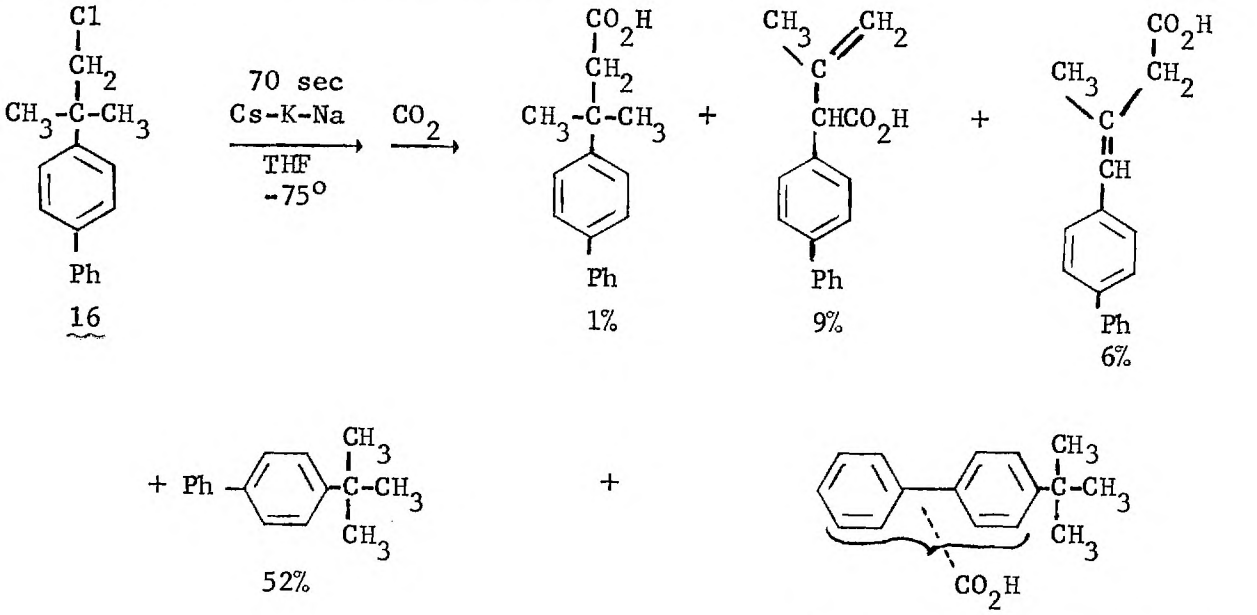
Our success in stabilizing the spiro anion 2 relative to the open anion 1 by two airs of gem-dimethyl groups as in 5 encouraged us to examine the "gem-dimethyl effect" r Thorpe-Ingold effect[7] in greater detail in our carbanionic system. Is one set of em-dimethyl groups as in 18 adequate to stabilize the spiro anion sufficiently for letection by carbonation techniques? Does [1,2] migration of the p-biphenylyl groups ccur in both of the dimethyl derivatives 17 and 20 below? To answer these questions

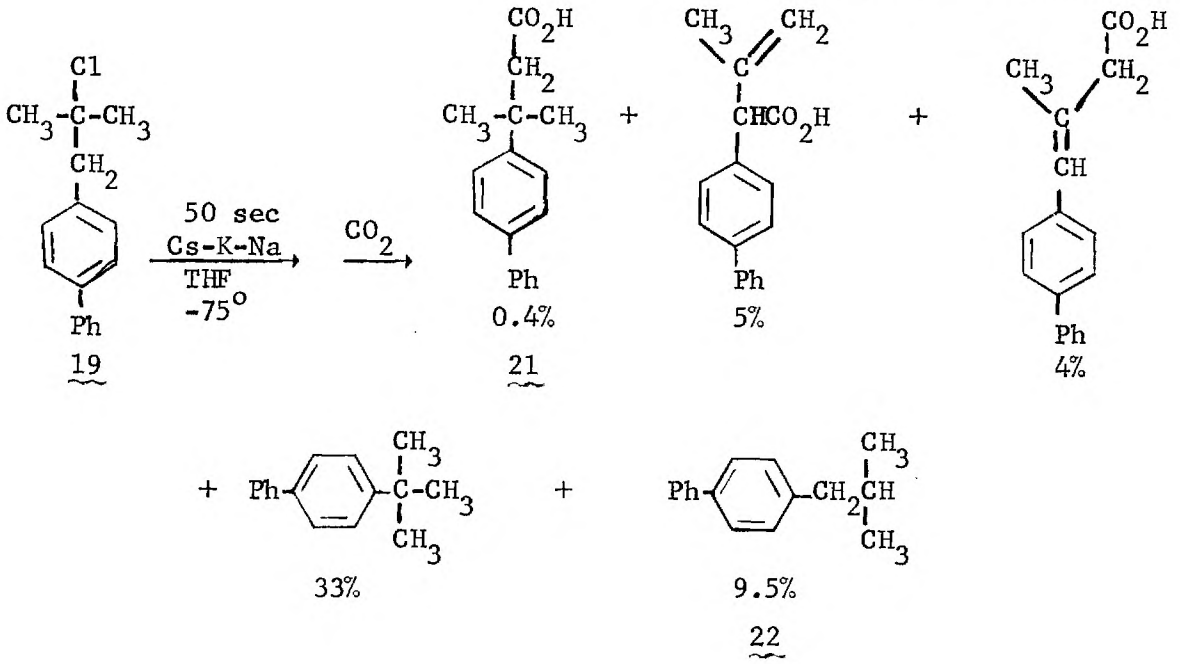


[6] A. Maercker and J. D. Roberts, J. Am. Chem. Soc., 88, 1742 (1966).

[7] See G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N.Y., 1956. pp 460-469; B. Capon and S. P. McManus, "Neighboring Group Participation," Vol. 1, Plenum Press, New York and London, 1976, pp 58-70.

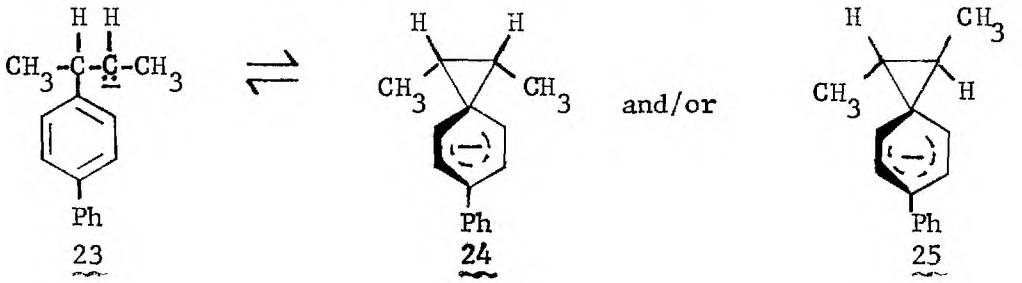
:he two chlorides 16 and 19 were synthesized and allowed to react with Cs-K-Na alloy
rith the results as summarized in the schemes below.





Neither chloride 16 nor 19 gave any detectable spiro carboxylic acid. While chloride 16 evidently underwent α-elimination with rearrangement of the p-biphenylyl group in a carbenoid intermediate, followed by metallation to give olefinic acids, no evidence for a rearrangement of the type 17 → 18 → 20 was obtained. In contrast chloride 19 gave rise to a small amount of the rearranged acid 21 and an appreciable amount of the rearranged hydrocarbon 22. Evidently the rearrangement 20 → 18 → 17 occurs but not the reverse process. Most of the rearranged product 17 is protonated

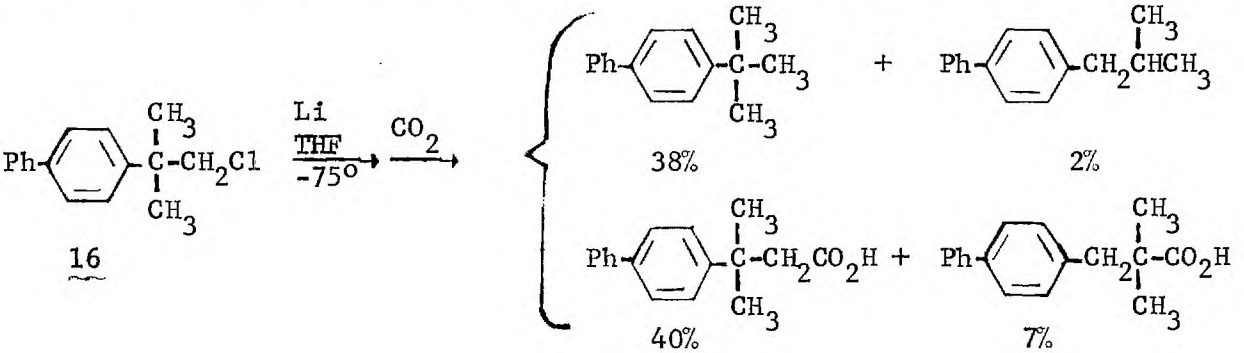
ıy the solvent (or other acid such as the alkyl chloride) prior to carbonation. Ie conclude that the gem-dimethyl groups in 20 facilitate rearrangement of the ırganocesium compound to 17 doubtlessly via the spiro anion 18. Also the primary ırganocesium compound 17 is thermodynamically more stable than either the tertiary ırganocesium compound 20 or the spiro anion 18. The destablization of carbanions (organoalkali compounds) by methyl groups is rather well documented[8] for reactions ın liquid solution although the theoretical reason(s) for such destabilization is not ıell agreed upon. Two pairs of gem-dimethyl groups as in 5 appear necessary for ıtabilization of the spiro anion relative to open forms. It should be emphasized that, ıt present, it is not known whether two methyl groups situated as in 24 or 25 would be



23 24 25

ıble to stablize the spiro anion relative to the open anion 23.

The reaction of halides 16 and 19 with lithium metal in tetrahydrofuran at -75° ıs of interest. The results are summarized below. The amount of rearrangement for



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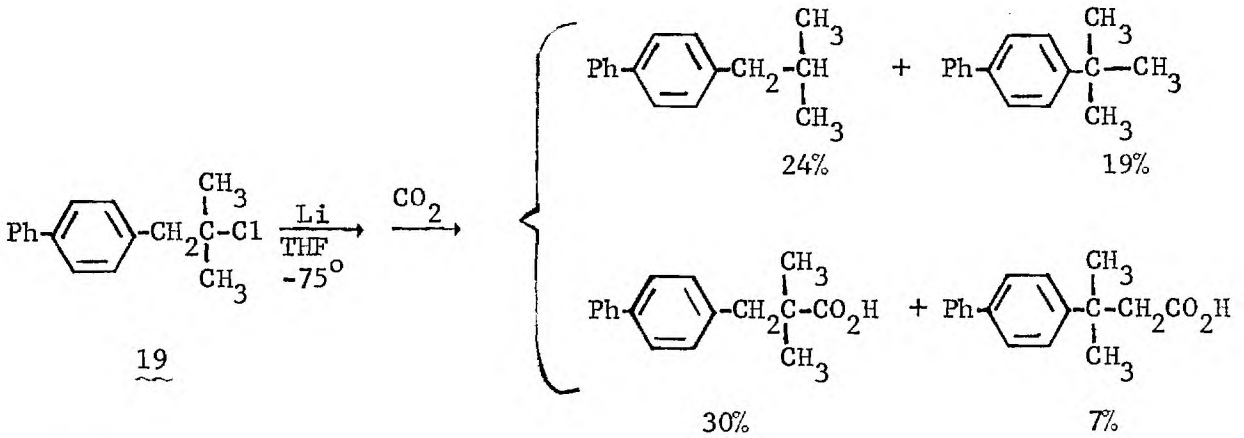
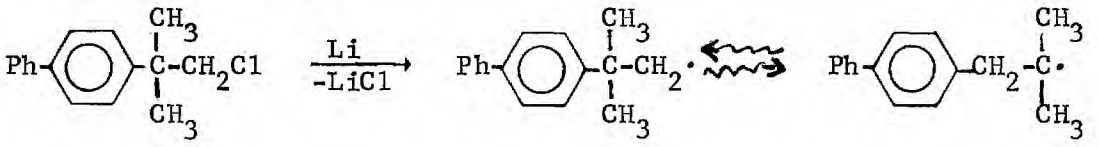


19

[8] D. J.Cram, "Fundamentals of Carbanion Chemistry," Academic Press, Inc., N.Y., N.Y., 1965, Chapter I.

reaction of halides 16 and 19 with lithium did not increae with increase in reaction time nor did the amount of rearrangement from halide 16 increase with increase in reaction temperature as shown by analyses for the volatile products listed in the above reaction summaries. Also when the reactions of halides 16 and 19 with lithium were run in THF containing a little tert-butyl alcohol the amount of rearrangement was not appreciably reduced. The organolithium compounds from chlorides 16 and 19 do NOT rearrange upon standing and the rearrangements observed are NOT rearrangements of carbanions but evidently rearrangements of free radicals formed during reaction at the lithium surface, e.g.



ther examples of rearrangements of radicals during reactions of organic chlorides with ithium metal have been reported[9] from our laboratories.

. [1,2] Migration of Phenyl during Preparation of Grignard Reagents

In experiments directed toward preparation of an authentic sample of acid for use s a standard in the analysis of products from rearrangement of an organoalkali metal ompound, we discovered that a phenyl group migrates partially during the preparation of he Grignard reagent from 5-chloro-4,4-diphenyl-1-pentene. In fairly extended studies henyl groups were also found to under [1,2] migration during preparation of Grignard eagents from 2-chloro-1,1,1-triphenylethane and 1-chloro-2,3,4-triphenylpropane. The rignard reagent itself once prepared from these halides does not undergo detectable earrangement. The observed phenyl migration, therefore, occurs during formation of he Grignard reagent, likely by way of radicals formed at the surface of the magnesium etal just as we have observed for reactions of chlorides with lithium metals. Our esults on phenyl migration during preparation of Grignard reagents have now been ublished in detail[10].

. [1,2] Migrations of Phenyl and Acetylene Groups in Reactions of 1-Chloro-5,5-dimethyl-,2-diphenyl-3-pentyne and 5-Chloro-4,4-diphenyl-2-pentyne with Alkali Metals

While [1,2] rearrangements of vinyl groups in organoalkali compounds and Grignard eagents have been known for some time, apparently only one example of migration of an acetylene group in a Grignard reagent has been reported.[11] We have found that 5-chloro-4,4-diphenyl-2-pentyne (26) reacts with lithium metal at -78° to give the expected organolithium product 27 which undergoes

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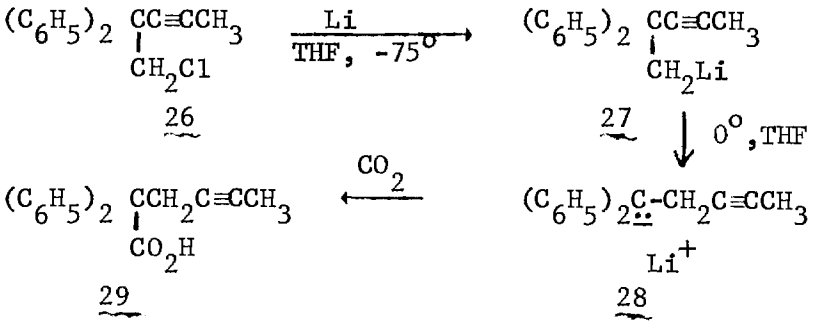
E. Grovenstein and Y.-M. Cheng, Chem. Commun., 101 (1970); E. Grovenstein, Jr., and J.-U. Rhee, J. Am. Chem. Soc., 97, 769 (1975).

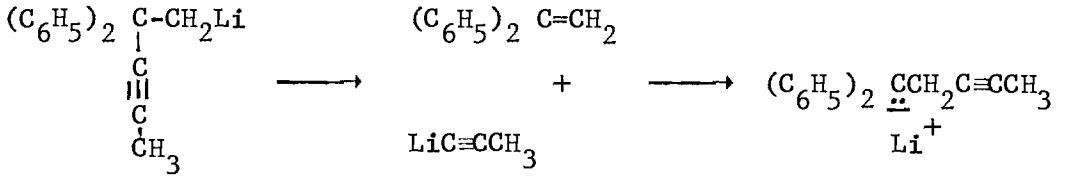
[10] E. Grovenstein, Jr., A. B. Cottingham, and L. T. Gelbaum, J. Org. Chem., 43, 3332 (1978).

[11] E. Grovenstein, Jr., Angew. Chem. Int. Ed. Eng., 17, pp 320-323 (1978); E. A. Hill, J. Organometal. Chem., 91, 123-271 (1975).

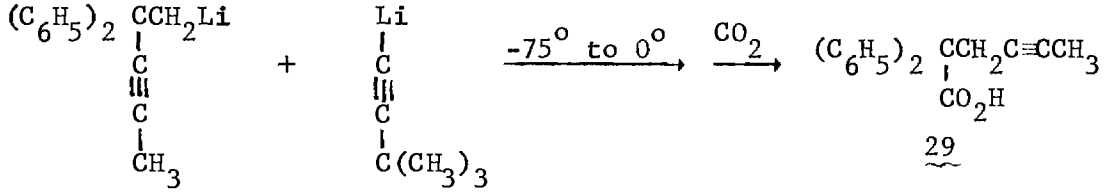


1,2] migration of the $-C\equiv CCH_3$ group upon warming to 0° to give 28 which was haracterized by carbonation to yield 29.

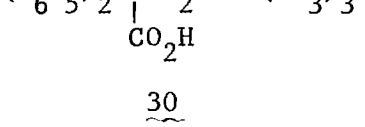
One possible mechanism for rearrangement of 27 would be by an elimination-readdition rocess outlined below:



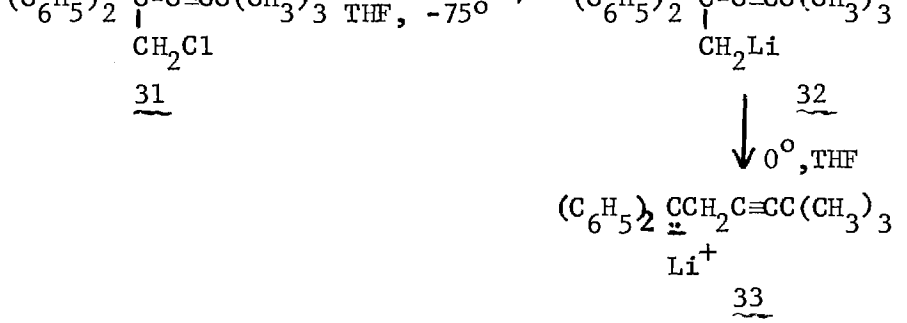
f the above mechanism were valid, it should be possible to intercept the intermediate iphenylethylene with another organolithium reagent such as $LiC\equiv CC(CH_3)_3$. Hence the est below has been carried out:



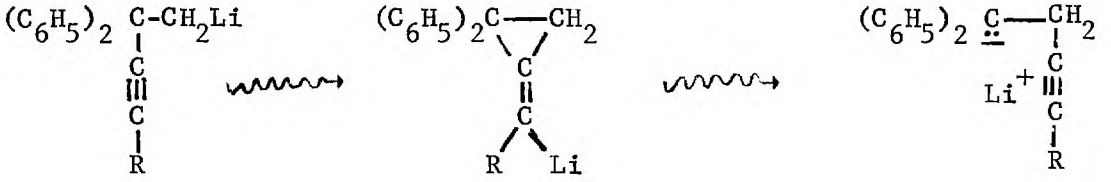
owever, only the usual rearrangement product 29 was obtained and none (<1%) of the -butylacetylene-incorporation product 30 could be detected.



That indeed a t-butylacetylene group is able to under a [1,2] rearrangement like he methylacetylene group of 27 was demonstrated by preparation and rearrangement of 2 to 33 under conditions analogous to those used for 27.

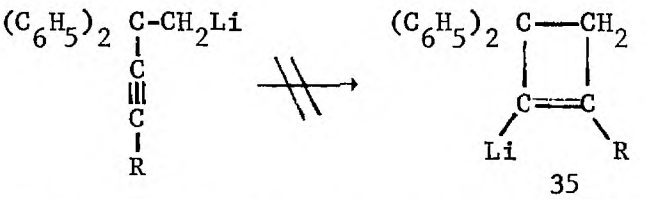


The most likely mechanism for the observed [1,2] migration of the acetylene groups in our organolithium compounds is by way of intermediate 34. This mechanism is



34

analogous to that accepted for migration of vinyl and aryl groups; however, the ring closure to 34 is an example of an 3-exo-digonal process which is disfavored by Baldwin's rules[12]. These rules would favor instead the 4-endo-digonal ring closure to 35 which, however, would not appear capable of leading to the observed products 28 and 33.

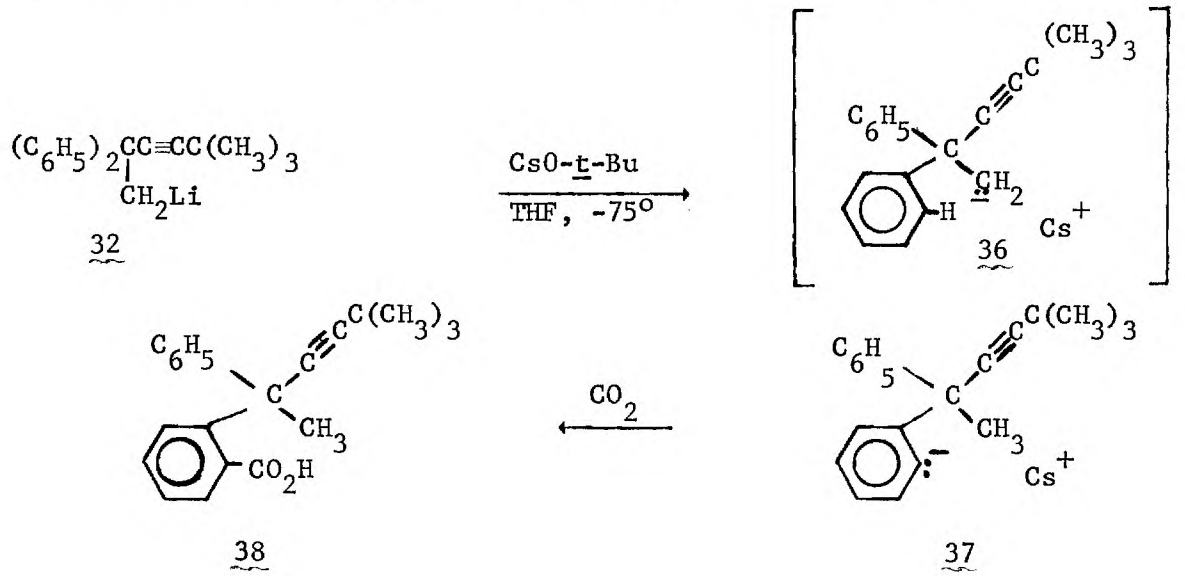


35

To probe the role played by the lithium cation in the above rearrangements of acetylene groups the organolithium compound 32 was treated with CsO-t-Bu at -75° with the aim of making the corresponding organocesium compound according to the general metathetical process shown in the following equation:

$$RLi + CsO\text{-}t\text{-}Bu \rightarrow RCs + LiO\text{-}t\text{-}Bu$$

In fact CsO-t-Bu catalyzed a new rearrangement of 32 evidently to the ortho metallation product 37. The structure of 37 rests upon the spectroscopic properties of its product of

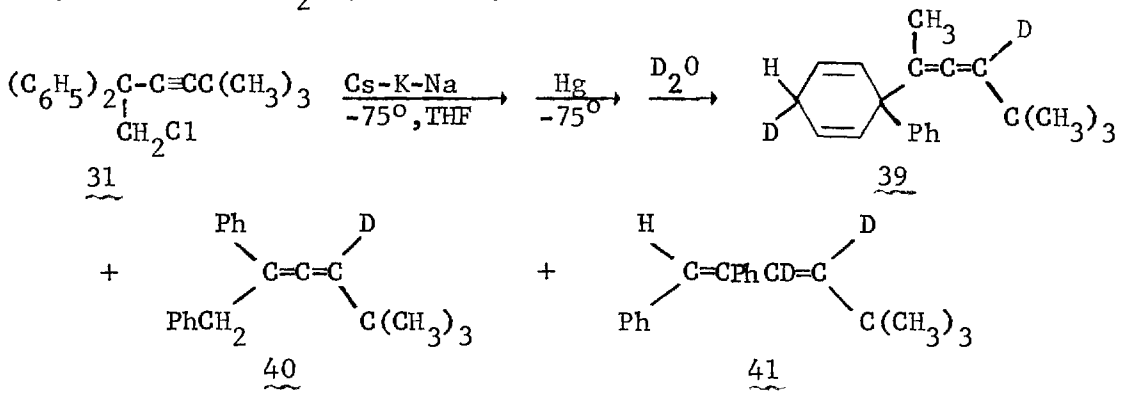


38 37

[12] J. E. Baldwin, J. Chem. Soc. Chem. Comm., 734 (1976).

arbonation 38; while the structure of 38 is likely correct, in view of some results ith Cs-K-Na alloy described below, it needs confirmation.

The putative organocesium compound 36 was made also by reaction of the corresponding hloride 31 with Cs-K-Na alloy at -75°; treatment with mercury to remove excess alloy nd decomposition with D_2O gave the products shown below.

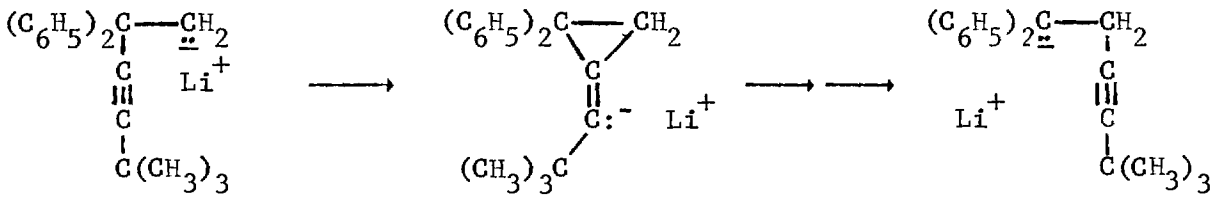


31 39 40 41

he ratio of 39:40:41 was approximately 40:30:30.

The products 39-41 may be accounted for by Scheme 1 (see page 12a). The organocesium ompound 42 is given the same structure as that 36 formed by way of the corresponding rganolithium compound 32. Yet 42 and 36 give different products! This is explained n the basis that 36 is formed initially as a solvent separated or loose ion pair; herefore, 36 is highly reactive and stabilizes itself by interaction with the nearest cidic proton which happens to be one in an ortho position of the two neighboring phenyl roups. Organocesium compound 42 formed by reaction of the chloride 31 with cesium lloy is evidently formed initially as a tight ion pair (contact ion pair). Species 2 is therefore longer lived than 36 and survives long enough to under [1,2] migration of the phenyl group or to extract a proton from anion 43 or from the solvent. It is notable that whereas the organolithium compound 32 undergoes only [1,2] migration f the acetylene group, the organocesium compound 42 undergoes only [1,2] migration of the phenyl group. That cesium as counter cation ends to favor migration of phenyl over other groups relative to lithium as counter ation has now been demonstrated in three cases: phenyl versus benzyl migration[13], henyl versus allyl migration[14], and the present phenyl versus acetylene migration.

Our explanation for the cation effect upon the present rearrangements is that rganolithium compound 32 rearranges in a tight ion pair via species 51 and 52 to he delocalized product 53. The reason why the tight ion pair with lithium (51)

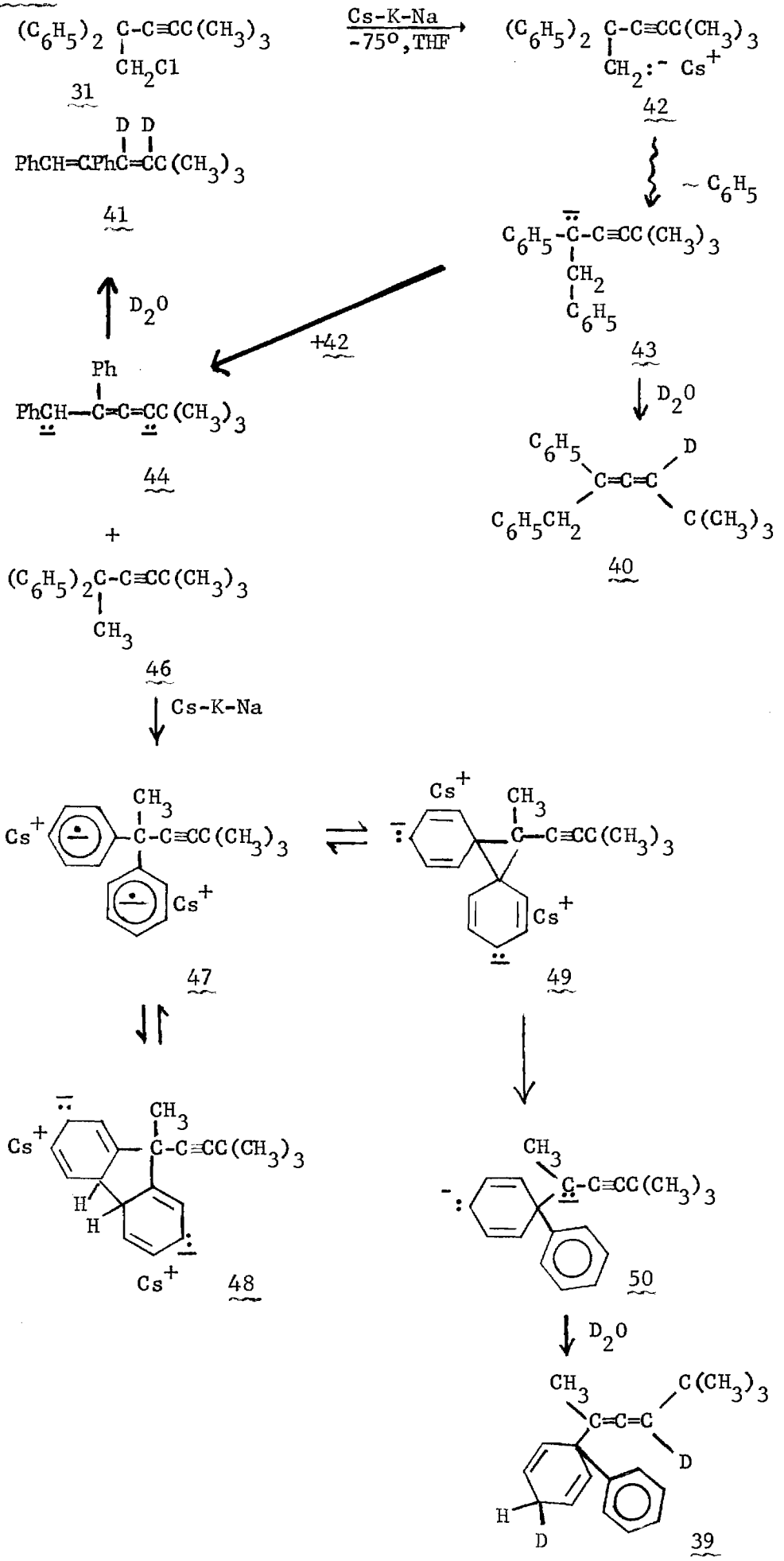


51 52 53

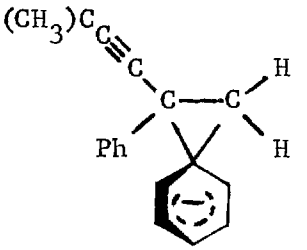
[13] E. Grovenstein, Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975).

[14] E. Grovenstein, Jr., and A. B. Cottingham, J. Am. Chem. Soc., 99, 1881 (1977).

cheme 1



gives migration of the acetylene group whereas the tight ion pair with cesium (42) gives migration of the phenyl group depends upon the fact that lithium cation has an ionic radius (0.60Å) about the size of the covalent radius of carbon (0.77Å) whereas cesium cation has an ionic radius (1.69Å) about the size of the radius of a benzene ring (1.40Å for the ring of carbon nuclei). The net result of electrostatic and covalent forces of attraction between these alkali metal cations and their oxygen anions appears to be that small lithium cations interact better with localized anions as in 51 and 52 than with delocalized anions such as 54 (which



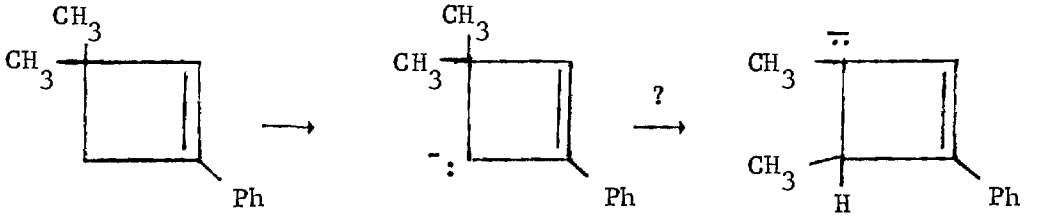
54

is the intermediate or transition state for phenyl migration) whereas large cesium cations interact better with the large delocalized anion 54 than with the localized anionic charge of 51 and 52.

The origin of product 39 as shown in Scheme 1 is discussed in Part II, "Reactions of Cesium and Cesium Alloys with Aromatic Hydrocarbons."

D. Search for [1,2] Migration of Methyl in Cyclobutenyl Anions

Previous unpublished work in our laboratory had as its goal study of possible [1,2] migration of methyl in the anion 56 whose synthesis was sought via reaction of olefin 55 with strong bases. This goal was frustrated by various alternative reactions, addition



55 56

of the base (e.g. n-butyllithium + tetramethylethylenediamine to the olefinic bond and possible metallation of the vinylic position or the aromatic ring of 55.

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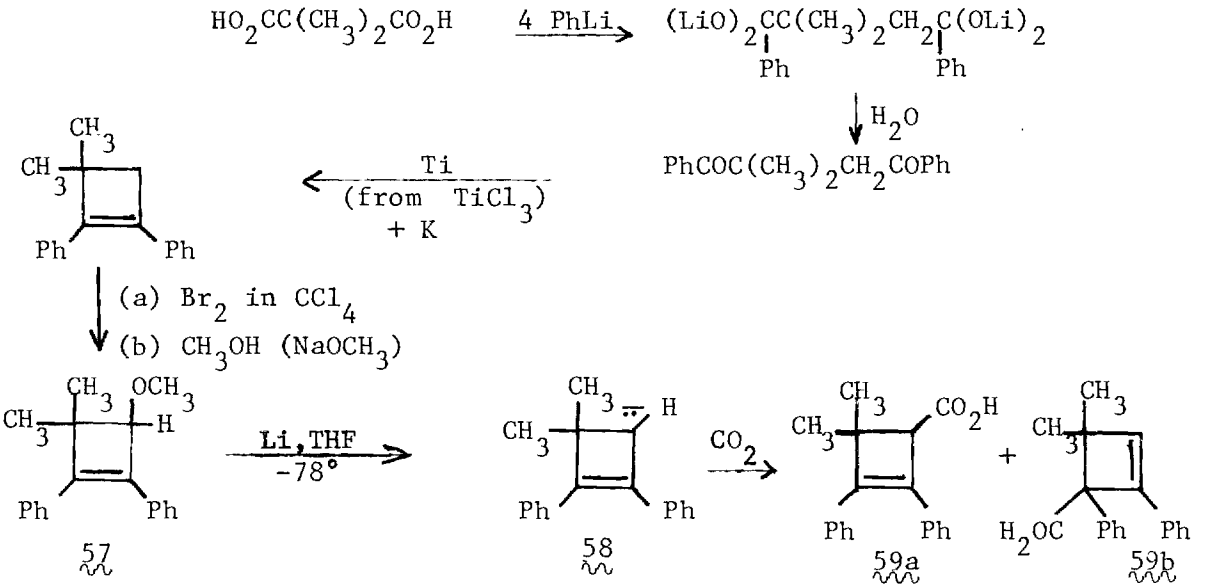
[15] E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, J. Org. Chem., 37, 1281 (1972).

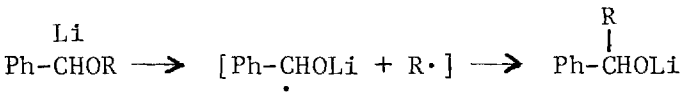
In new work the vinylic hydrogen of 55 has been replaced by a phenyl group which should th make vinylic metallation impossible and increase the stability of the allylic anion 56. so the allylic anion has been sought by ether cleavage of 57 with alkali metals rather an by metallation. The following synthesis of 58 has been successfully achieved.



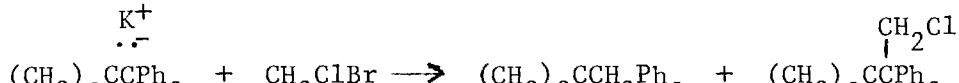
The mixture of carboxylic acids from carbonation of the carbanion, both after its eparation at -78°C and after warming to 0° for three hours, has been shown to contain a, likely 59b, and compounds of longer GC retention time (possibly dicarboxylic acids, lymers and/or their pyrolysis products). Full identification is complicated by thermal stability of 59a and 59b; however, the results to date suggest that methyl migration 58 is NOT a facile process.

Search for [1,2] Migration of tert-Butyl in 2,2-Diphenyl-3,3-dimethylbutyl Anion

Lansbury, Schöllkopf, and coworkers[16] have suggested that the Wittig rearrangement of hers proceeds via dissociation into a radical pair:



so it was noted that a tert-butyl group migrated 2080 times more readily than a methyl oup in lithiobenzyl alkyl ethers. The ready migration of tert-alkyl groups in Wittig her rearrangements suggested the desirability of looking for corresponding migrations simpler carbanions without heteroatoms. Hence we have studied the rearrangement of 2-diphenyl-3,3-dimethylbutyllithium. The synthesis of this compound posed some experintal difficulties. The usual synthesis by reaction of the corresponding chloride with thium metal was made impossible by the unavailability of the pure chloride. Attempts make the chloride by reaction of 2,2-dimethyl-1,1-diphenylpropyl anion (60) with



60 61 62

ther dichloromethane or bromochloromethane gave mostly the hydrocarbon 61 and little the desired chloride 62. Efforts to separate 62 from 61 by chromatography on silica

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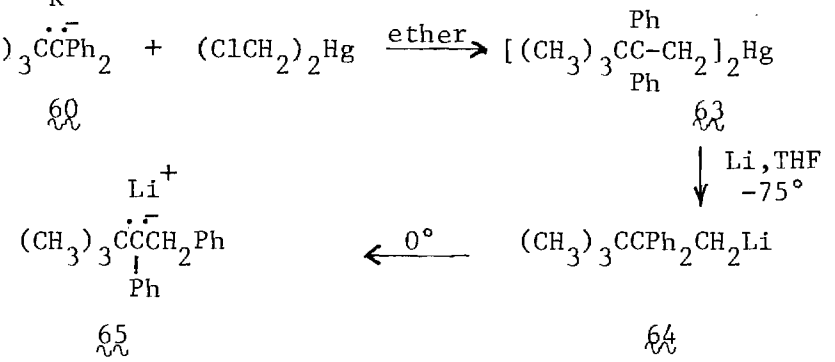
P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, J. Am. Chem. Soc., 88, 78 (1966); V. Schöllkopf, Angew. Chem. Int. Ed. Eng., 9, 763 (1970).

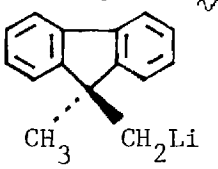
el were vitiated by decomposition of 62 (evidently both steric acceleration and
ıenyl participation in 62 make this halide unusually reactive via mechanism S_N1).
ıccessful synthesis of 2,2-diphenyl-3,3-dimethylbutyllithium was finally accomplished
Scheme 2 which utilizes the novel reaction of the anion 60 with bis(chloromethyl)-

Scheme 2

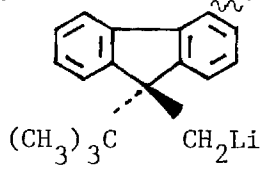


ercury to give the product of S_N2 displacement on carbon 63 and negligible amounts of
ıe hydrocarbon 61. The organolithium compound 64 when warmed to 0° in THF underwent
1,2] migration of phenyl and no observable migration of tert-butyl just as the methyl
ıalog 66, according to Zimmerman and Zweig,[17] underwent phenyl migration without observable
ethyl migration. Thus neither a tert-butyl nor a methyl group has sufficient migratory

ptitude to compete with phenyl in rearrangement of these organolithium compounds without
eteroatoms. This is of course not to say that, if migration of the phenyl group could be
etarded, migration of tert-butyl would be unobservable. For example, Eisch and Kovacs[18]
ound that organolithium compound 68, closely related to 66, underwent neither migration of



68



69

aryl nor methyl; evidently aryl migration in 68 involves (for the usual, low energy pathway) a highly strained spiro intermediate or transition state. Hence, in absence of aryl migration, tert-butyl migration may yet be observable in 69.

F. Rearrangement of 2,2-Diphenyl-3-p-tolylpropyl Anion

While the rearrangement of benzyl in 2,2,3-triphenylpropyllithium is most simply explained as proceeding via an elimination and readdition of benzyllithium, Grovenstein and Wentworth[19] pointed out that this rearrangement could proceed via cleavage to a radical pair as has been suggested for Wittig ether rearrangements[16]:

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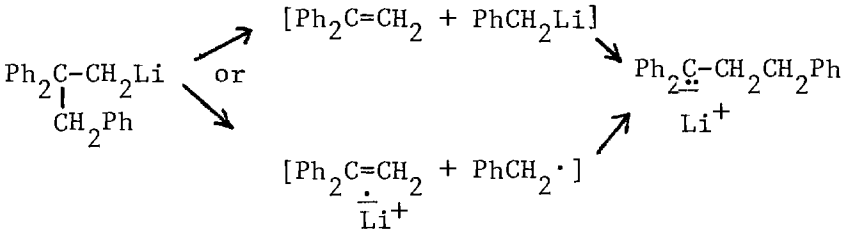
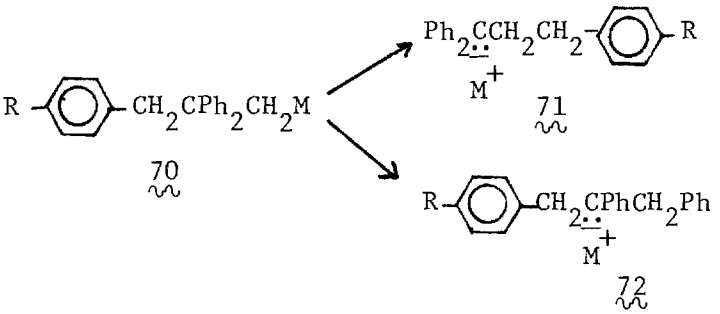
7 H. E. Zimmerman and A. Zweig, J. Am. Chem. Soc., 83, 1196 (1961).

8 J. J. Eisch and C. A. Kovacs, J. Organomet. Chem. 25, C33 (1970).

9 E. Grovenstein, Jr., and G. Wentworth, J. Am. Chem. Soc., 85, 3305 (1963); ibid, 89, 1852 (1967).



Since subsequent work[20] showed that the 2,2,3-triphenylpropyl anion can (under appropriate conditions) undergo competitive migration of phenyl via a concerted process, a method was now apparent to distinguish between the two possible fragmentation processes. Namely, if a para substituent is placed in the benzyl group, it should be possible to accelerate or retard the migration of benzyl relative to phenyl dependent upon whether the group stabilizes or destabilizes anions versus radicals. A para methyl group should retard formation of the benzyl anion[21] but accelerate somewhat formation of the benzyl radical[22] while leaving the rate of phenyl migration nearly unaffected. The results from our experiments are recorded below.



Relative Yields

M	Temp., °C	R = H[20] 71:72	R = CH_3 71:72
Li	0°	99:<1	99:<1
K	-75°	63:37	25:75
Cs	-75°	25:75	<1:99

The results show that rearrangement of the compound with a para methyl group parallels that of the unsubstituted compound; but that in every case in which the ratio of 71 to 72 is measurable, it is smaller for the compound with the para methyl substituent. In other words the para methyl substituent has reduced the amount of benzyl migration relative to phenyl migration. The results are therefore in agreement with benzyl migration occurring by elimination and readdition of benzyl anion rather than benzyl radical. Also the results continue to demonstrate an interesting cation effect[20] in rearrangement of 70. The large difference in the ratio of 71 to 72 even on going from potassium to cesium is notable and stresses that the organometallic chemistry of cesium may frequently be different in a synthetically useful manner from that of the other alkali metals.

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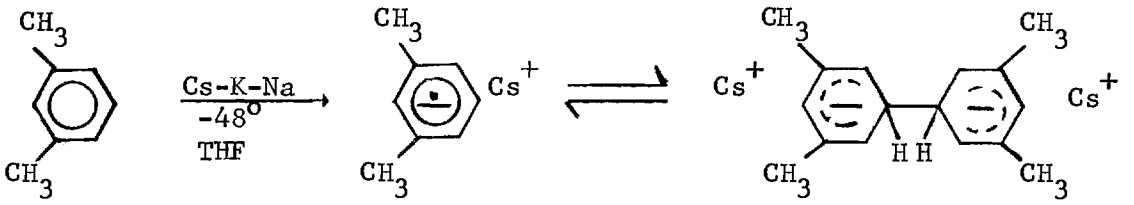
20 E. Grovenstein, Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975).

21 G. Gau and S. Marque, J. Am. Chem. Soc., 98, 1538 (1976); A. Streitwieser, Jr., and J. H. Hainmons, Prog. Phy. Org. Chem., 3, 59-65 (1965).

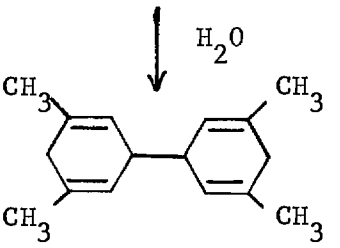
22 W. A. Pryor, "Free Radicals," McGraw-Hill Co., New York, 1966, pp 169, 173, and 175; C. Rüchardt, Angew. Chem. Int. Ed. Eng., 9, 830 (1970); S. Dinctürk, R. A. Jackson, and M. Townsend, J. C. S. Chem. Comm., 172 (1979).

'ART II. Reactions of Cesium and Cesium Alloys with Aromatic Hydrocarbons

Our work upon reaction of cesium and Cs-K-Na alloy with benzene and toluene has ıow been published[23] and, therefore, will not be discussed further here. In similar ıanner m-xylene reacts with excess Cs-K-Na alloy in THF at -48° to give the radical ınion 73 which largely dimerizes to 74 as judged by the dimeric hydrocarbon 75 which ːs obtained in 55% yield as a beautifully crystalline compound upon siphoning the ːeaction mixture into ice water.

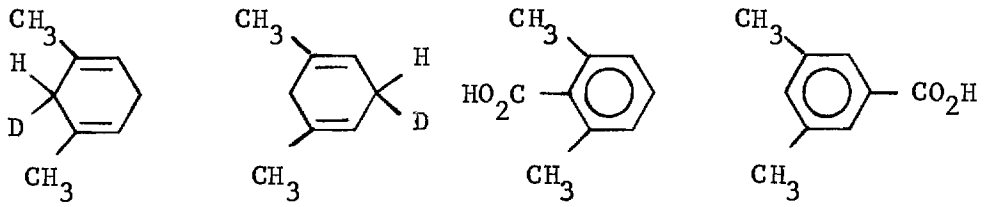


73 74



75

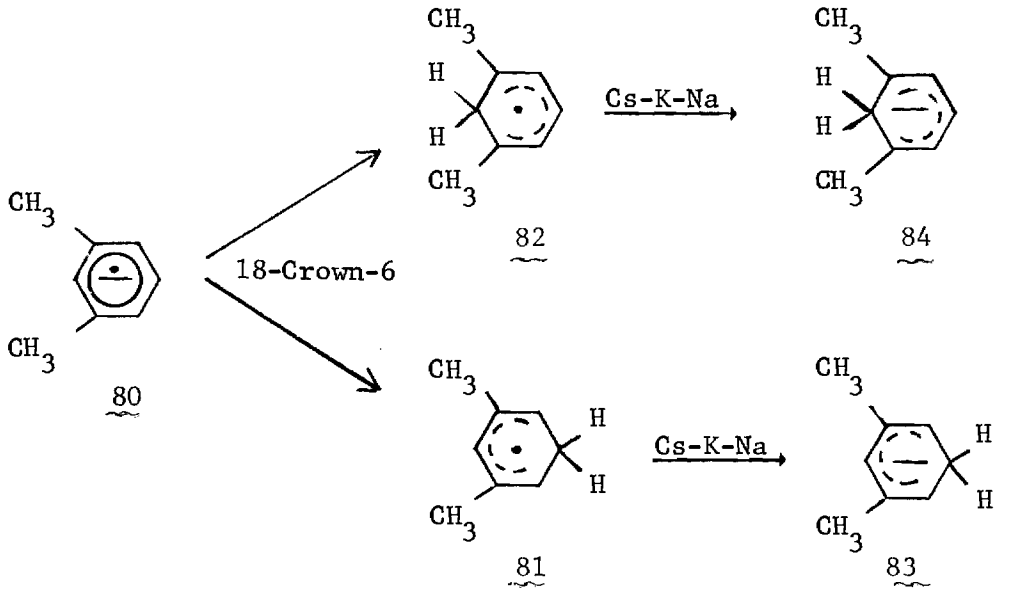
In contrast reaction of m-xylene with Cs-K-Na alloy in THF in presence of one ıolar equivalent of 18-crown-6 gave on protonation after some three hours only ıonomeric hydrocarbons. For a reaction which was quenched with D_2O, 64 mole % of ː,5-dihydro-m-xylene and 33 mole % of unreacted m-xylene was obtained. According ːo ^1H and ^{13}C NMR analysis, the 2,5-dihydro-m-xylene was monodeuterated and consisted ›f a 1 : 3.74 ratio of 76 to 77. In another run with two molar equivalents of .8-crown-6 per mole of m-xylene, the acidic product from carbonation and dehydrogenation ːonsisted of a 1: 3.86 ratio of 78 to 79. These data are in good argeement with the



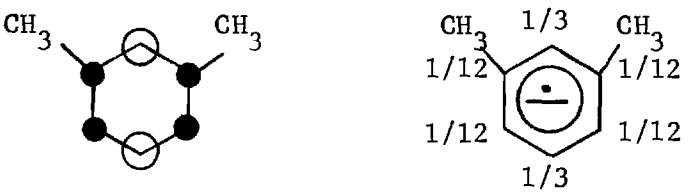
76 77 78 79

ːonclusion that 18-crown-6 protonates the radical anion 73 to give about a 1 : 3.8 ıixture of radicals 81:82 which are reduced to the corresponding ratio of anions 83 : 84.

23 E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).



Note that the chemistry of m-xylene radical anion can be interpreted in terms of the HOMO structure 85 or the charge distribution 86[24]. Dimerization and protonation



85 86

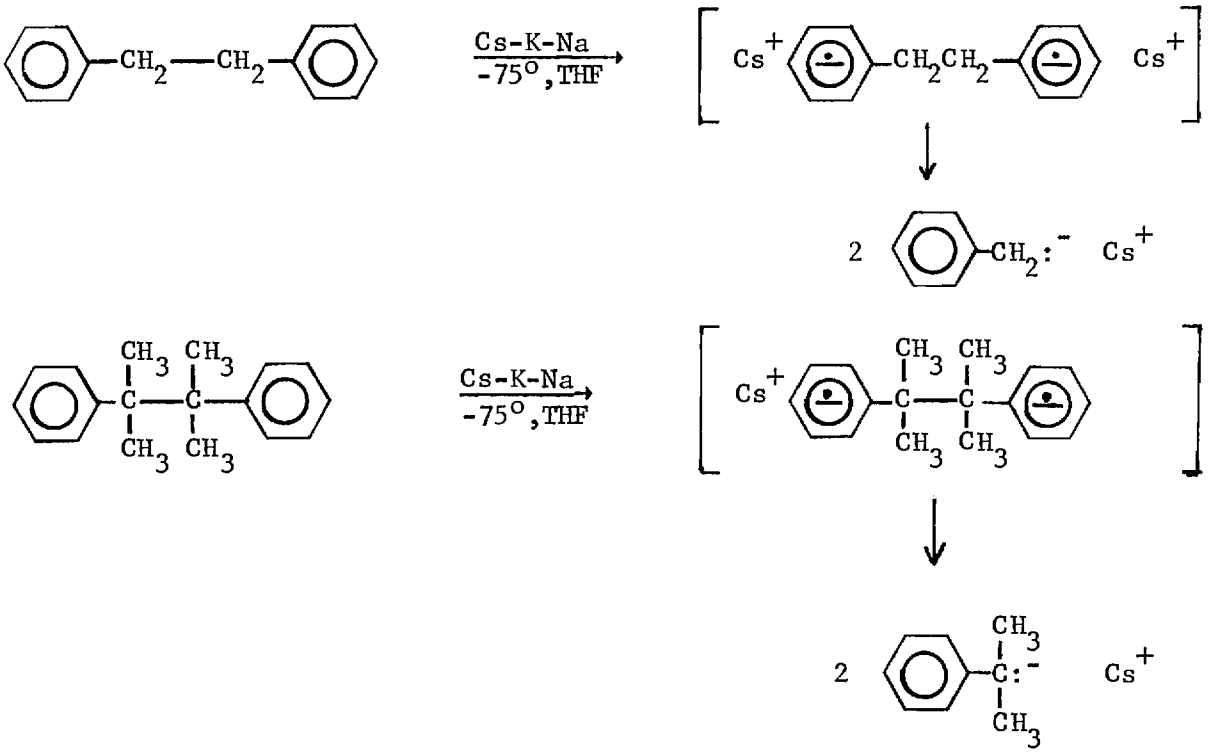
of the radical anion would be expected to take place at the positions of highest electron-spin density or charge density, hence at positions 2 or 5. Dimerization takes place preferentially at the 5 positiion since this process leads to the most stable anion 74 where the methyl groups are at the nodal positions in the HOMO (and hence destabilize the anions as little as possible). Protonation in contrast occurs preferentially at the 2-position since this process leads to the most stable radical 82 where the methyl groups are all at centers of high spin density (and hence stabilize the radical as much as possible). The higher regiospecificity in dimerization than in protonation accords with the larger effect of methyl groups in destabilizing anions than in stabilizing radicals in solution. The theoretical explanation of this substituent effect is poorly understood but the effect is of considerable importance to free radical and carbanion chemistry.

In similar experiments with benzene and Cs-K-Na alloy in THF at -43° in presence of two molar equivalents of 18-crown-6 for five hours, the products of carbonation indicated that somewhat less than half of the benzene radical anion was protonated by 18-crown-6 in contrast to complete protonation of m-xylene radical anion under

[24] See L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, N. Y., N. Y., 1966, p. 255.

ilder conditions. These comparative results may be understood on the basis that ıethyl groups destabilize radical anions and increase their rate of protonation y 18-crown-6.

The cleavage reactions shown below have been observed to take place readily at ow temperature likely by way of intermediate dianions. The yields of benzylic anions



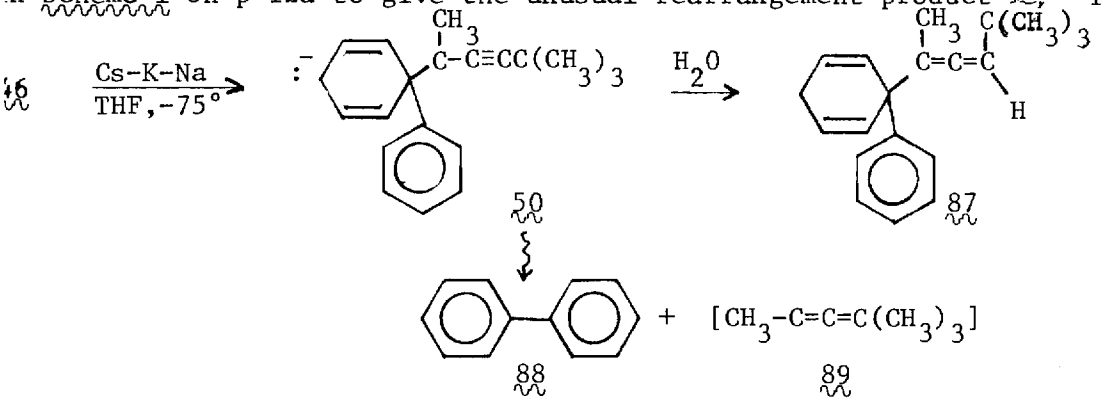
are quantitative. These reactions would appear to be of synthetic utility.

Experiments on the reaction of 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (31) with

$$ClCH_2C(Ph_2)C{\equiv}CC(CH_3)_3 \longrightarrow CH_3C(Ph_2)C{\equiv}CC(CH_3)_3$$

31 46

s-K-Na alloy in THF at -75° suggested that 31 was partially converted to the hydrocarbon 6 which reacted with excess Cs-K-Na alloy according to the processes shown in detail n Scheme 1 on p 12a to give the unusual rearrangement product 50. This suggestion has



ıow been confirmed by subjecting the hydrocarbon 46 to the reaction conditions of the chloride 31 and obtaining a hydrocarbon 87 identical to that obtained from the chloride.

In addition biphenyl (88) accompanied the formation of 87 and may readily be interpreted as arising from fragmentation of anion 50 which is the precursor of 87. The rearrangement of the hydrocarbon 46 to the anion 50 is to our knowledge without precedent. This rearrangement is a good example of the powerful reducing potential of cesium alloy and of the unique chemistry which cesium provides at very low reaction temperatures.

PART III. Publications of Work Supported by the Present National Science Foundation Grant

(1) "Carbanions. 17. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," E. Grovenstein, Jr., and A. B. Cottingham, J. Am. Chem. Soc., 99, 1881 (1977).

(2) "Carbanions. 18. Spiro Anions from Reactions of 2- and 3-p-Biphenylylalkyl Chlorides with Cesium-Potassium-Sodium Alloy," J. A. Bertrand, E. Grovenstein, Jr., P.-C. Lu, and D. VanDerveer, J. Am. Chem. Soc., 98, 7835 (1976).

(3) "Carbanions. 19. Reactions of Cesium or Cesium-Potassium-Sodium Alloy with Benzene and Toluene," E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).

(4) "Aryl Migrations in Organometallic Compounds of the Alkali Metals," by E. Grovenstein, Jr., in Advances in Organometallic Chemistry, F. G. A. Stone and R. West, Editors, Academic Press, New York, N. Y. Vol. 16, pp 167-210 (1977).

(5) "Phenyl Migration during Preparation of Grignard Reagents," E. Grovenstein, Jr., A. B. Cottingham, and L. T. Gelbaum, J. Org. Chem., 43, 3332 (1978).

(6) "Skeletal Rearrangements of Organoalkali Metal Compounds," E. Grovenstein, Jr., Angew. Chem., 90, 317-336 (1978); Angew. Chem. Int. Ed. Engl., 17, 313-332 (1978).

(7) "Carbanions.20. Rearrangement in Reactions of 5-Chloro-4,4-diphenyl-2-pentyne, 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne, and 5,5-Dimethyl-2,2-diphenyl-3-hexyne with Alkali Metals," E. Grovenstein, Jr., K.-W. Chiu, and B. B. Patil, manuscript nearly complete.

(8) "Carbanions.21. Reactions of 2- and 3-p-Biphenylylalkyl Chloride with Alkali Metals; Preparation of Labile Spiro Anions," E. Grovenstein, Jr., and P.-C. Lu, manuscript in preparation.

(9) "Carbanions.22. Cleavages of Hydrocarbons by Cs-K-Na Alloy," E. Grovenstein, Jr., D. E. Quest, and D. Sengupta, manuscript in preparation.*

10) "Carbanions.23. Rearrangements of 2,2,3-Triphenylpropyl and 2,2-Diphenyl-3-p-tolylpropyl Alkali Metal Compounds," E. Grovenstein, Jr., R. E. Williamson, and T. E. Brantley, manuscript in preparation.

Three theses have been completed under the present grant:

Pang-Chia Lu, "Spirocyclic Intermediates in the Rearrangements of Organoalkali Compounds," Ph.D. Thesis, Georgia Institute of Technology, September, 1977.

Dean E. Quest, "Reactions of Cesium Alloys with Aromatic Hydrocarbons and Alkyl Chlorides," Ph.D. Thesis, Georgia Institute of Technology, October, 1977.

* This work was in part supported by a grant from the Petroleum Research Fund of the the American Chemical Society.

Troy E. Brantley, "The Rearrangement of 2,2-Diphenyl-3-p-tolylpropyllithium," M. S. Thesis, Georgia Institute of Technology, August, 1979.

APPENDIX III

Facilities Available

An adequate amount of air-conditioned, well-equipped laboratory space will be made available by the School of Chemistry. The special facilities include two glove boxes for organometallic reactions, a Varian E-104 Electron Paramagnetic Resonance Spectrometer with variable temperature probe, two 60 MHz NMR machines, one JEOL PFT-100 MHz NMR Spectro meter (Fourier transform machine with probes for C-13 and H-1), Cary Recording Spectrometer, several Perkin-Elmer Infrared Spectrometers, an Hatachi Perkin-Elmer RMU-7L Mass Spectrometer, a Varian MAT-112S Medium Resolution GC Mass Spectrometer (equipped for both chemical and electron impact ionization) interfaced with Varian MAT-SS200 Data System. The aid of a laboratory equipped for single-crystal x-ray diffraction analysis utilizing a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator is accessible in the School of Chemistry. A WM-300 Brooker, superconducting, Fourier transform, NMR spectrometer with multinuclear capabilities including ^{2}H, ^{7}Li, and ^{133}Cs should be installed by the summer of 1980 and should prove useful in the proposed studies. Finally the services of glass blowers, a machinist, electronic repairmen, and technicians to operate the mass spectrometers and the 100 and 300 MHz NMR spectrometers are all available in the School of Chemistry.

APPENDIX VI

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Institute of Technology 225 North Ave.,N.W. Atlanta, Georgia 30332	Chemistry Div. Chemical Dynamics Program	CHE-7602720
	4. Award Period From 1-1-76 To 6-30-80	5. Cumulative Award Amount $146,000

6. Project Title

"Chemistry of Carbanions"

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

The objective of this work was to explore some of the basic chemistry of carbanions with special attention being devoted to the topic of rearrangement of carbanions. By means of deuterium-labeling studies and with alcohols to serve as "traps" for carbanions, it has been demonstrated that 2-p-biphenylyl-1,1,2-trimethylpropyl-lithium and -cesium undergo facile [1,2] migration of the p-biphenylyl group even at -75°C. In the case of the cesium compound the equilibrated product contains about 80% of an intermediate spiro anion in which the p-biphenylyl group bridges two carbons of the side chain,but with the lithium compound only the open form of the organoalkali compound is detectable. Likewise [1,2] migration of p-biphenylyl occurs in 1,1-dimethyl-2-p-biphenylylethylcesium but not in 2-methyl-2-p-biphenylylpropylcesium. While [1,2] migrations of the p-biphenylyl group occur in reactions of 1-chloro-2-methyl-2-p-biphenylylpropane and 2-chloro-2-methyl-1-p-biphenylylpropane with lithium, these rearrangements occur via intermediate free radicals formed during the reaction of the chlorides with lithium metal not in the organolithium products themselves. Rearrangements of intermediate free radicals are also responsible for the [1,2] migration of phenyl observed in the products (Grignard reagents) of reaction of 2-chloro-1,1,1-triphenylethane and 1-chloro-2,2,3-triphenylpropane with magnesium.

We have observed the first [1,2] migrations of acetylenic groups in 2,2-diphenyl-3-pentynyllithium and 5,5-dimethyl-2,2-diphenyl-3-hexynyllithium. In contrast 5,5-dimethyl-2,2-diphenyl-3-hexynylcesium undergoes preferential [1,2] migration of phenyl rather than of the acetylenic moiety. 2,2-Dimethyl-3,4-diphenyl-3-cyclobutenyllithium, has been prepared but no evidence for [1,2] or [1,4] migration of methyl in this anion has been observed. Likewise 2,2-diphenyl-3,3-dimethylbutyllithium does not undergo [1,2] migration of the t-butyl group but instead preferential [1,2] migration of phenyl. When phenyl migration is rendered difficult by steric constraints as in 9-lithiomethyl-9-t-butylfluorene, eliminative cleavage of t-butyl as isobutylene occurs to give 9-methylfluorenyllithium. Liquid Cs-K-Na alloy in THF at -75°C dimerizes benzene and some of its alkyl derivatives to give dianions, quantitatively cleaves dibenzyl and derivatives to benzyl anions, and rearranges 5,5-dimethyl-2,2-diphenyl-3-hexyne to a novel dianion.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses		✓			
b. Publication Citations		✓			
c. Data on Scientific Collaborators		✓			
d. Information on Inventions				✓	8-80
e. Technical Description of Project and Results		✓			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
Dr. Erling Grovenstein, Jr.	Erling Grovenstein, Jr.	6-30-80

NSF Form 98A (5-78) Supersedes All Previous Editions

Form Approved OMB No. 99R0013

a. ABSTRACTS OF THESES

SPIROCYCLIC INTERMEDIATES IN THE REARRANGEMENTS OF ORGANOALKALI COMPOUNDS

A THESIS

Presented to

The Faculty of the Graduate Division

by

Pang-Chia Lu

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

Georgia Institute of Technology

September, 1977

SUMMARY

The purpose of this research is to study the possible rearrangements of some organoalkali compounds (or carbanions) of lithium and cesium and to detect any reactive spiro intermediates. While spiro anions have long been suggested as intermediates or transition states in [1,2] migrations of aryl groups in organoalkali reactions, their presence has not been directly detected or observed.

Reaction of 3-p-biphenylyl-1-chloropropane, m.p. 32-33°, with Cs-K-Na alloy of eutectic composition in THF at -75° for 33 seconds gave a dark red solution which on carbonation yielded 36% of 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid (III), 14% of p-biphenylylacetic acid, 3% of 2-p-biphenylylbutanoic acid, and 4% of 4-p-biphenylylbutanoic acid. The yield of acid III decreased with time; the intermediate spiro anion had a half-life of about 13 minutes and disappeared on standing or raising the temperature of the reaction mixture. In contrast, reaction of the chloride with lithium in THF at -75° gave 3-p-biphenylylpropyllithium which was not appreciably rearranged even at -20°. Treatment of this organolithium reagent with CsO-t-Bu or KO-t-Bu in THF gave 3-p-biphenylylpropylcesium (or -potassium) which underwent 1,3-proton shift to form the more stable 1-p-biphenylylpropylcesium (or -potassium). Reaction of the chloride with Cs-K-Na in presence of 18-crown-6 also gave 1-p-biphenylylpropylcesium as the major product but also gave a good yield of the spiro acid III.

Though cyclopropyl and cyclobutyl rings have about the same total ring strain, reaction of 2-p-biphenylyl-1-chloropropane with Cs-K-Na alloy in THF at -75° for one minute gave less than 1% (if any) of the desired spiro anion even though some 60% of the starting chloride had been consumed.

Reaction of 2-p-biphenylyl-1-chloro-2-methylpropane, m.p. 63-64°, with Cs-K-Na alloy in THF at -75° for 70 seconds gave after carbonation a complex mixture of products of which the major volatile products were identified as 20% of 2-p-biphenylyl-3-methyl-3-butenoic acid (VIII), 2.5% of 3-p-biphenylyl-3-methylbutanoic acid (IX), 3% of 4'-t-Bu-3-biphenylcarboxylic acid (X), and 10% of 4-p-biphenylyl-3-methyl-3-butenoic acid (XI). No products directly derived from a spiro anion were obtained. The olefinic acids VIII and XI are believed to be formed by α-elimination followed by proton abstraction from the olefin. Reaction of the chloride with lithium metal in THF at -75° gave mainly 2-p-biphenylyl-2-methylpropyllithium together with 10 to 15% of 2-p-biphenylyl-1,1-dimethylethyllithium. There was no isomerization of these organolithium compounds into one another under the reaction conditions tested. When this reaction was repeated in presence of t-BuOH, the same ratio of rearranged to non-rearranged products was found. These facts suggest that the rearranged organolithium compound was formed via rearrangement of an intermediate free radical.

Reaction of 1-p-biphenylyl-2-chloro-2-methylpropane, m.p. 97-97.5°, with Cs-K-Na alloy in THF at -75° gave besides some β-elimination products, a 79 to 21 ratio of rearranged to unrearranged products. Speculately, 2-p-biphenylyl-1,1-dimethylethylcesium was first formed,

then cyclized and re-opened to give the more stable 2-p-biphenylyl-2-methylpropylcesium. When the same reaction was run in THF in presence of MeOH, a 33 to 67 ratio of rearranged to unrearranged products were found. This result agrees with the idea that it is mostly the carbanion which is undergoing rearrangement and which is trapped prior to rearrangement by addition of MeOH. Reaction of the same chloride with lithium in THF at -75° gave relative yields of 67% of 2-p-biphenylyl-1,1-dimethylethyllithium and 33% of 2-p-biphenylyl-2-methylpropyllithium. When this lithium reaction was repeated in presence of t-BuOH, a 77 to 23 ratio of unrearranged to rearranged product was formed. Since there was no further rearrangement detected after the two organolithium compounds were formed, the possible pathway for the formation of the rearranged organolithium compound could be partly via a spiro radical and partly via a spiro anion only loosely bound to a lithium cation.

Reaction of 3-p-biphenylyl-2-chloro-2,3-dimethylbutane, m.p. 110-111°, with lithium in THF at -75° gave after carbonation 3-p-biphenylyl-2,2,3-trimethylbutanoic acid (XX). In contrast, reaction of this chloride with Cs-K-Na alloy in THF at -75° gave 7% of 3-p-biphenylyl-2.2.3-trimethylbutanoic acid (XX) and 28% of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (XXI) along with considerable nonvolatile acid. 1,1,2,2-Tetramethyl-6-phenylspiro-[2.5]octadienyl anion (XXXV) is regarded as a precursor of the acid XXI and has a half-life of about 22 minutes in THF at -75°. The open form 2-p-biphenylyl-1,1,2-trimethylpropylcesium (XXXIV) has the same half-life as XXXV. This and other evidence suggest that XXV and XXXIV are in mobile equilibrium. When the starting chloride was labeled

primarily with deuterium in the methyl groups nearest the chlorine, the open carboxylic acid XX from carbonation showed extensive deuterium label in the methyl groups nearest the biphenylyl group in about the amount expected for equilibration of the label in an intermediate carbanion. For a mobile equilibrium between XXXIV and XXXV, certain electrophilic reagents may attach one of the isomeric anions more readily than the other; this is believed to be the reason why reaction with trimethylsilyl chloride or dimethyl sulfate yielded only open chain trimethylsilylation or methylation product.

While the equilibrium between XXXIV and XXXV with cesium as cation the mixture consists of a 1:4 ratio respectively of the anions; with lithium as counter ion in THF only the open form 2-p-biphenylyl-1,1,2-trimethylpropyllithium was present according to the result of carbonation. Evidently lithium cation prefers to interact with the localized anion since such interaction can lead to the usual covalent organolithium compound.

REACTIONS OF CESIUM ALLOYS WITH AROMATIC HYDROCARBONS AND ALKYL CHLORIDES

A THESIS

Presented to

the Faculty of the Graduate Division

by

Dean E. Quest

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

Georgia Institute of Technology

October, 1977

SUMMARY

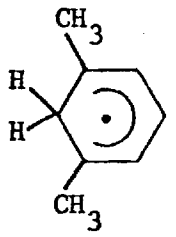
The purpose of this research was to investigate the reactions of cesium-potassium alloy and cesium-potassium-sodium alloy with aromatic hydrocarbons and alkyl chlorides. The compounds investigated were benzene, toluene, t-butylbenzene, m-xylene, p-xylene, biphenyl, diphenylmethane, 2,2-diphenylpropane, 1,1,1-triphenylethane, bibenzyl, 1,2-di-p-tolyethane, 2,3-dimethyl-2,3-diphenylbutane, 1,2,2-triphenylpropane, 1,3-diphenylpropane, cyclohexyl chloride, and 2,2,3-triphenylpropyl chloride.

Reaction of benzene with excess Cs-K-Na alloy at -45°C in THF produces cesium benzenide (I) as a black solid. After three hours at -45°C, dicesium 1,1-'dihydrobiphenylide (II), a yellow solid, is formed by the intramolecular coupling of I. Compound II upon protonation with water gave a 75.7 mole % yield of 1,1',4,4'-tetrahydrobiphenyl (III) whose structure was ascertained by ^{1}H NMR, ^{13}C NMR, and mixture gc injections with an authentic sample of III.

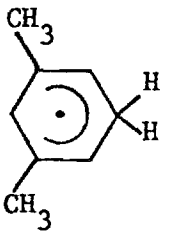
Reaction of toluene with excess Cs-K-Na alloy at -45° in THF produces initially cesium toluenide (IV) as a black solid. After three hours at -45°C, dicesium 3,3'-dimethyl-1,1'-dihydrobiphenylide (V), a yellow solid is formed by the intermolecular coupling of IV. Compound V upon protonation with water gave a 56.3 mole % yield of 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl (VI) whose structure was ascertained by ^{1}H NMR, ^{13}C NMR, UV, IR, MS, elemental analysis, and dehydrogenation. Dehydrogenation of

the dimeric products with excess DDQ gave 3,3'-dimethylbiphenyl (99.1%), 2,3'-dimethylbiphenyl (0.7%), and 2,2-dimethylbiphenyl (0.2%). Thus the dimerization of IV favors coupling of the radical anion at the position meta to the methyl group by 99.5%.

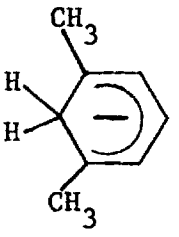
Reaction of m-Xylene with excess Cs-K-Na alloy at -48°C in THF produces initially cesium m-xylenide (VII) as a black solid. After three hours at -45°C, dicesium 3,3',5,5'-tetramethyl-1,1'-dihydrobiphenylide (VIII), a yellow solid, is formed by the intermolecular coupling of VII. Compound VIII upon protonation with water gave a 54.8 mole% yield of 3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl (IX) whose structure was ascertained by ^{1}H NMR, ^{13}C NMR, UV, IR, MS, elemental analysis, and dehydrogenation. In the presence of 18-crown-6 VII is quantitatively protonated to apparently form radicals X and XI, which are rapidly reduced by the alloy to anions XII and XIII respectively. Deuteration and carbonation of anions XII and XIII indicate that these



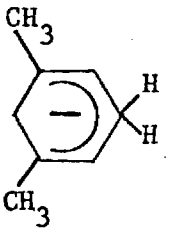
X



XI



XII



XIII

anions and their radical precursors are in a 3.8 : 1.0 ratio.

Both p-xylene and t-butylbenzene fail to react with Cs-K-Na alloy at -45°C in THF.

Reactions of bibenzyl with Cs-K-Na alloy at -75°C likely produces dicesium 1,2-diphenylethanide which rapidly cleaves to benzylcesium, the

latter after carbonation gives phenylacetic acid in nearly quantitative yield. Under these reaction conditions, the radical anions of 2,3-dimethyl-2,3-diphenylbutane and 1,2,2-triphenylpropane but not 1,2-di-p-tolylethane are quantitatively cleaved to give the appropriate benzyl anions.

Analysis of the cesium alloy for the reacting alkali metal in reaction of Cs-K alloy with benzene, 1,3-diphenylpropane, and 2,2-diphenylpropane at -20°C in THF or the reaction of Cs-K-Na alloy with benzene, toluene, 1,3-diphenylpropane, 1,2,1-triphenylethane, and 1,2,2-triphenylpropyl chloride at -45°C in THF shows that cesium metal is selectively removed from the alloy during reaction. Since both metals in Cs-K alloy can react with biphenyl or cyclohexyl chloride at 25°C in THF, analysis of the alloy under these conditions indicated that the ratio of cesium to potassium removed from the alloy was 10 : 1, a result which demonstrates the superior reducing ability of cesium metal in THF.

THE REARRANGEMENT OF

2,2-DIPHENYL-3-P-TOLYLPROPYLLITHIUM

A THESIS

Presented to

The Faculty of the Division of Graduate Studies

By

Troy Ellis Brantley

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

Georgia Institute of Technology

August, 1979

SUMMARY

The aim of this research is to study the mode of rearrangement of the benzyl group ($-CH_2C_6H_5$) in [1,2] migrations of organoalkali compounds.

1-Chloro-2,2-diphenyl-3-p-tolylpropyllithium reacts with lithium metal at -78°C to give 2,2-diphenyl-3-p-tolylpropyllithium, which upon carbonation is converted to 3,3-diphenyl-4-p-tolylbutanoic acid (I). Reaction of the same chloride at -78° with lithium metal yields, upon warming to 0° for one hour and carbonation, 2-2-diphenyl-4-p-tolylbutanoic acid (II). This acid results from a [1,2] shift of benzyl in 2,2-diphenyl-3-p-tolylpropyllithium to produce 1,1-diphenyl-3-p-tolylpropyllithium before carbonation.

Treatment of 2,2-diphenyl-3-p-tolylpropyllithium with potassium or cesium tert-butoxides results in a competitive [1,2] migration of benzyl and phenyl. Migration of benzyl gives the previously mentioned acid (II), while migration of phenyl yields a new acid, 2-benzyl-2-phenyl-3-p-tolylpropanoic acid (III). The potassium tert-butoxide catalyzed rearrangement gave 24.5% (II) and 75.5% (III). Catalysis by cesium tert-butoxide gave 0.5% (II) and 60.1% (III) with the remainder of the product being non-rearranged acid (I).

b. Publication Citations

Publications of Work Supported by the Present National Science Foundation Grant

(1) "Carbanions. 17. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds," E. Grovenstein, Jr., and A. B. Cottingham, J. Am. Chem. Soc., 99, 1881 (1977).

(2) "Carbanions. 18. Spiro Anions from Reactions of 2- and 3-p-Biphenylylalkyl Chlorides with Cesium-Potassium-Sodium Alloy," J. A. Bertrand, E. Grovenstein, Jr., P.-C. Lu, and D. VanDerveer, J. Am. Chem. Soc., 98, 7835 (1976).

(3) "Carbanions. 19. Reactions of Cesium or Cesium-Potassium-Sodium Alloy with Benzene and Toluene," E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).

(4) "Aryl Migrations in Organometallic Compounds of the Alkali Metals," by E. Grovenstein, Jr., in Advances in Organometallic Chemistry, F. G. A. Stone and R. West, Editors, Academic Press, New York, N. Y. Vol. 16, pp 167-210 (1977).

(5) "Phenyl Migration during Preparation of Grignard Reagents," E. Grovenstein, Jr., A. B. Cottingham, and L. T. Gelbaum, J. Org. Chem., 43, 3332 (1978).

(6) "Skeletal Rearrangements of Organoalkali Metal Compounds," E. Grovenstein, Jr., Angew. Chem., 90, 317-336 (1978); Angew. Chem. Int. Ed. Engl., 17, 313-332 (1978).

(7) "Carbanions.20. Rearrangement in Reactions of 5-Chloro-4,4-diphenyl-2-pentyne, 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne, and 5,5-Dimethyl-2,2-diphenyl-3-hexyne with Alkali Metals," E. Grovenstein, Jr., K.-W. Chiu, and B. B. Patil, accepted for publication in J. Am. Chem. Soc., should appear in September, 1980.

(8) "Carbanions.21. Reactions of 2- and 3-p-Biphenylylalkyl Chloride with Alkali Metals; Preparation of Labile Spiro Anions," E. Grovenstein, Jr., and P.-C. Lu, manuscript in preparation.

(9) "Carbanions.22. Cleavages of Hydrocarbons by Cs-K-Na Alloy," E. Grovenstein, Jr., D. E. Quest, and D. Sengupta, manuscript in preparation.*

(10) "Carbanions.23. Rearrangements of 2,2,3-Triphenylpropyl and 2,2-Diphenyl-3-p-tolylpropyl Alkali Metal Compounds," E. Grovenstein, Jr., R. E. Williamson, and T. E. Brantley, manuscript in preparation.

Three theses have been completed under the present grant:

Pang-Chia Lu, "Spirocyclic Intermediates in the Rearrangements of Organoalkali Compounds," Ph.D. Thesis, Georgia Institute of Technology, September, 1977.

Dean E. Quest, "Reactions of Cesium Alloys with Aromatic Hydrocarbons and Alkyl Chlorides," Ph.D. Thesis, Georgia Institute of Technology, October, 1977.

Troy E. Brantley, "The Rearrangement of 2,2-Diphenyl-3-p-tolylpropyllithium," M. S. Thesis, Georgia Institute of Technology, August, 1979, partially supported by NSF.

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* This work was in part supported by a grant from the Petroleum Research Fund of the American Chemical Society.

c. Data on Scientific Collaborators Supported by Present NSF Grant

Principal Investigator, Dr. Erling Grovenstein, Jr.:
supported 6 summer months (or half-time for 4 summers)

Post-doctoral Research Associates:

(1) Dr. Bhalchandra B. Patil: 17 months full-time support by NSF (also 9 months of support by the School of Chemistry as a half-time post-doctoral teaching assistant with half-time work on project).

(2) Dr. Kuen-Wai Chiu: 25 months full-time support by NSF (also 3-1/2 months of support by the School of Chemistry as a half-time post-doctoral teaching assistant with half-time work on project).

(3) Dr. Dibyendu Sengupta: 6 months full-time support by NSF (also 9 months of support by the School of Chemistry as a half-time post-doctoral teaching assistant with half-time work on project).

Graduate Student Research Assistants (Half-time during Academic Year, Full-time work during Summer):

(1) Edward J. Jeroski: 3 months

(2) Pang-Chiu Lu: 19 months

(3) Dean E. Quest: 21 months

e. Technical Description of Project and Results

Summary of Progress to Date upon "Chemistry of Carbanions"

NSF Grant CHE 76-02720 For Period Jan. 1, 1976 - June 30, 1980

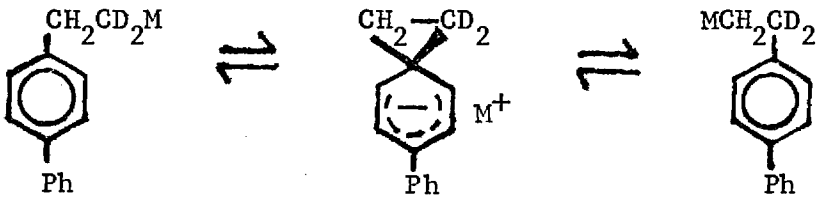
by Erling Grovenstein, Jr., Principal Investigator

I. Studies upon Rearrangements of Carbanions

The simplest reaction which a carbanion (i.e., an organoalkali metal compound) can undergo ld appear to be a molecular rearrangement. Since knowledge about the occurrence or non-urrence of such a reaction would appear necessary for successful procedures using carbanion synthetic reagents and because carbanions are the most useful of the three possible valent forms of carbon in organic syntheses, expecially for formation of new carbon-carbon ds, much of our effort has been directed toward learning the structural features and ction conditions necessary for rearrangements of carbanions.

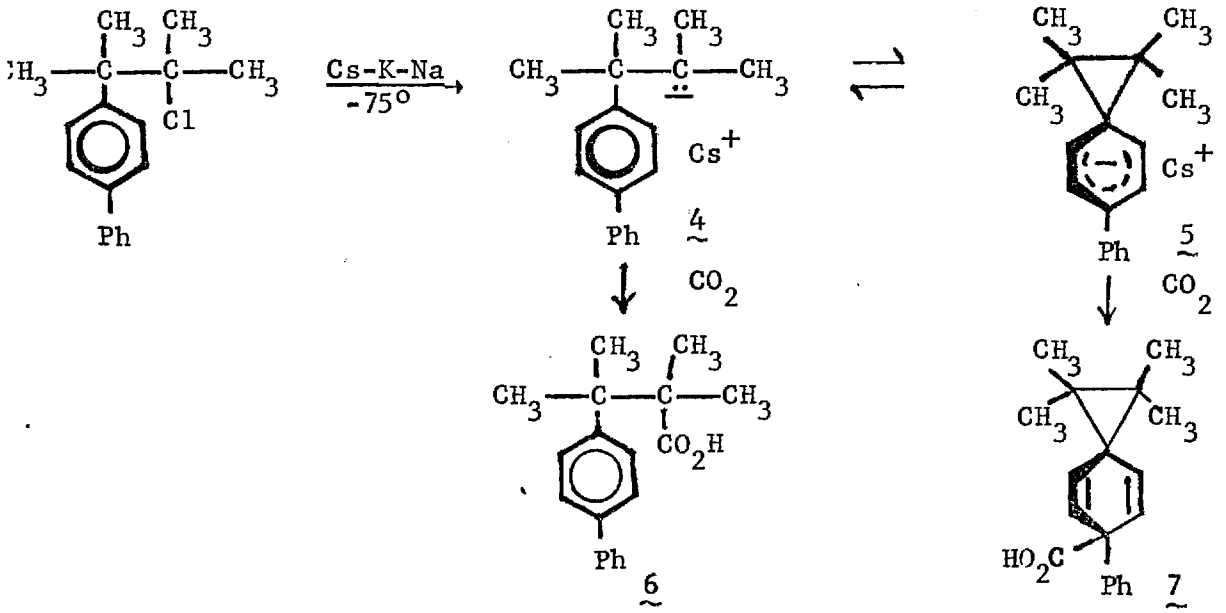
[1,2] Migration of p-Biphenylyl in 2-p-Biphenylylethyl Anions and Radicals

Spiro anions have long been suggested as intermediates or transition states in migrations aryl groups in organoalkali compounds. While 2-p-biphenylylethylpotassium and -cesium ergo ready rearrangement[1] (1 → 3) in tetrahydrofuran (THF), attempts to detect the ermediate spiro anion 2 in the reaction of 2-chloro-1-p-biphenylylethane with excess



1 2 3

-K-Na alloy in THF at -75° for one minute before carbonation indicated less than 1% (if any) the desired spiro anion in the reaction mixture even though most of the starting chloride l been consumed. In contrast reaction of 2-p-biphenylyl-3-chloro-2,3-dimethylbutane :h Cs-K-Na alloy in THF at -75°C for one minute gave after carbonation some 28% of the :ro acid 7 and 7% of 3-p-biphenylyl-2,3,3,-trimethylbutanoic acid 6 as shown in the ıeme below. This work has been published in a preliminary communication[2] which includes

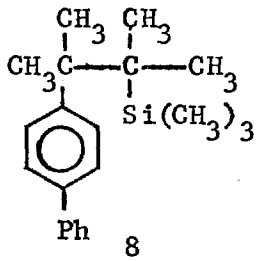


E. Grovenstein,Jr., and Y.-M. Cheng, J. Am. Chem. Soc., 94, 4971 (1972).

J. A. Bertrand, E. Grovenstein, Jr., P. C. Lu, D. Van Derveer, J. Am. Chem. Soc., 98, 7835 (1976).

o an x-ray diffraction study to confirm the structure of 7.

In unpublished work the mobile equilibrium between 4 and 5 has been established by eral techniques. First the half-life of the spiro anion 5 and of the open anion 4 each about 22 minutes in THF at -75°C as determined from the results of carbonation. s finding is surprising for anions of such dissimilar structure as 4 and 5 but can readily understood if 4 and 5 are in mobile equilibrium. Second the mixture of anocesium compounds 4 and 5 when allowed to react with trimethylsilyl chloride or ethyl sulfate gives only the open derivatives 8 and 9 respectively and no spiro



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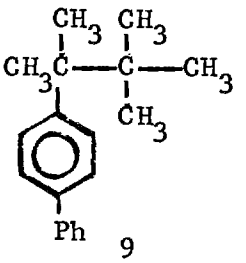
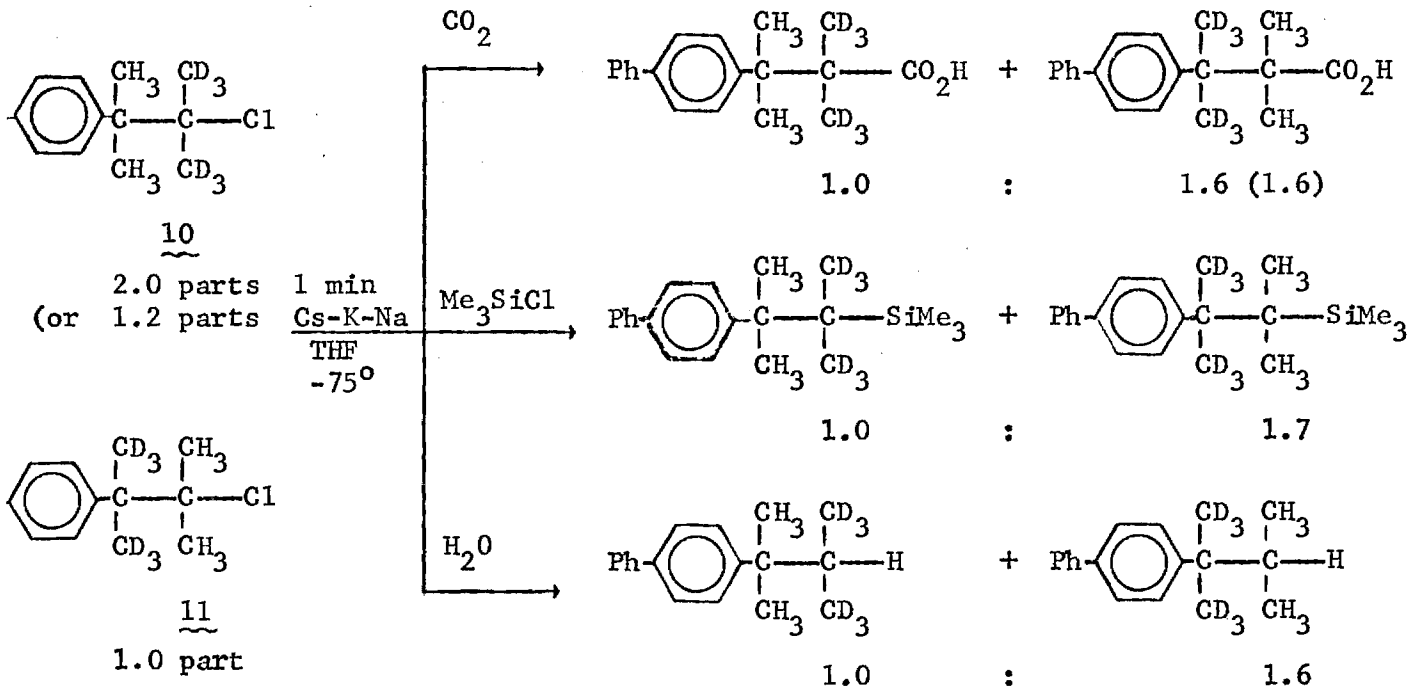


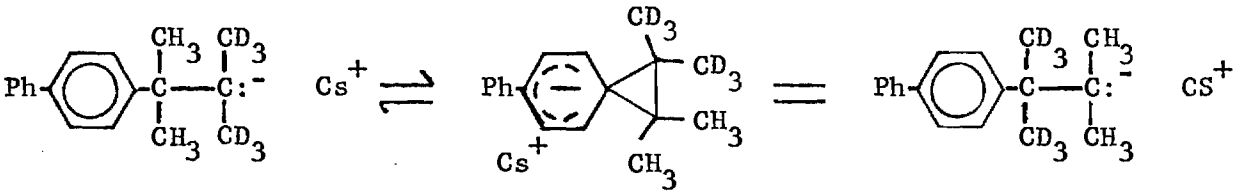
9

ducts. These results are understandable on the basis that, for a mobile equilibrium ⇌ (5), certain reagents may attack one of the isomeric anions more readily than the er. In particular the less reactive dimethyl sulfate and trimethylsilyl chloride ely react preferentially with the localized anion 4 rather than with the delocalized on 5 while the more reactive carbon dioxide reacts unselectively with both 4 and 5. ally confirmation comes from studies with the 2.0 to 1.0 mixture of the deuterium eled chlorides 10 and 11 respectively which gave the product ratios with various ctrophiles as shown in the scheme below:



e that even when the ratio of 10 to 11 was 1.2 to 1.0 the product ratio on carbonation s identical to that starting with the usual 2.0 to 1.0 ratio of 10 to 11. In summary

. experiments with the deuterium-labeled chloride confirm that cesium alloy reacts h the chloride to give the spiro anion 12 which is in mobile equilibrium with the n anions 13 and 14. If the results of carbonation can be relied upon to measure position of equilibrium, the equilibrium may be depicted as shown below:

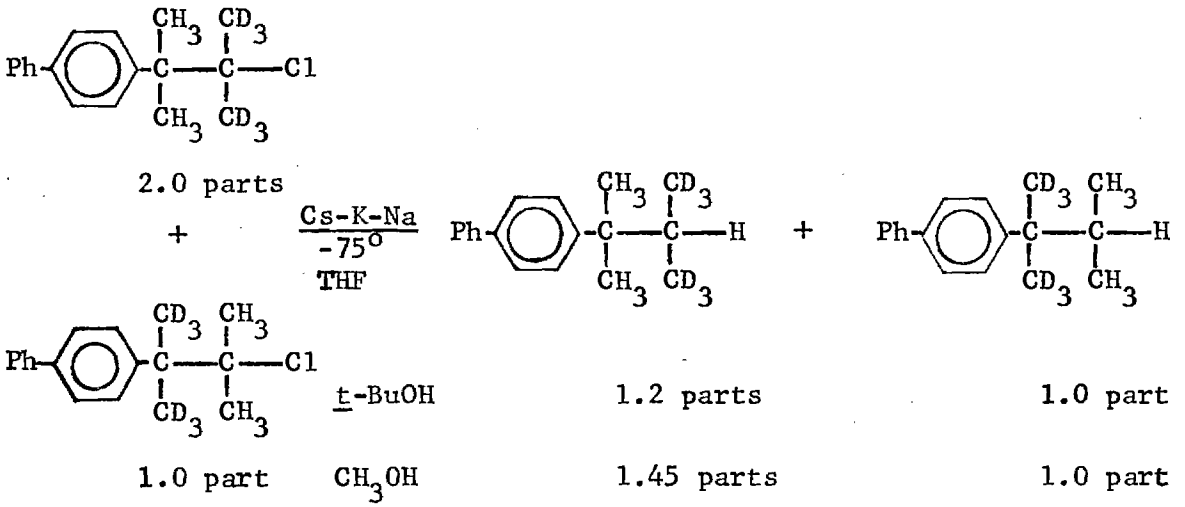


13 12 14

1.0 part 9 parts 1.6 parts

ratio of 14 : 13 of 1.6 : 1.0 reflects a large secondary deuterium isotope effect and is the correct magnitude expected for such an effect by analogy to that quoted[3] for $(CD_3)_3N$ equilibrium with $(CH_3)_3N^+H$ in the gas phase and may be explained in terms of a recent ory[4] of anionic hyperconjugation involving the methyl groups.

The question arises does the rearrangement outlined above in terms of the anions 12 14 in fact occur in intermediate free radicals rather than carbanions. We swer this question in the negative on the basis, in part, that it is possible to "trap" reactive intermediate prior to rearrangement by carrying out the reaction with Cs-K-Na loy in THF in presence of small amounts of alcohols as shown below. Note that as



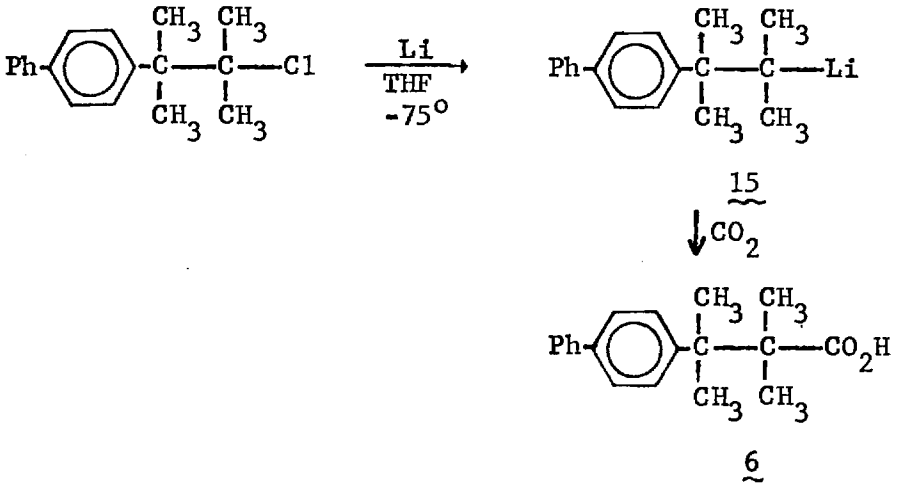
acidity of the alcohol decreases from methanol to tert-butyl alcohol the amount rearrangement decreases. The alcohols should be good "traps" for carbanions but ould be less effective in donating hydrogen atoms to free radicals than the solvent trahydrofuran[5]. Hence the formation of carbanions from our alkyl chloride precedes e rearrangement step itself.

J. F. Wolf, J. L. Delvin, P. J. DeFrees, R. W. Taft, and W. F. Hehre, J. Am. Chem. Soc., 98, 5097 (1976).

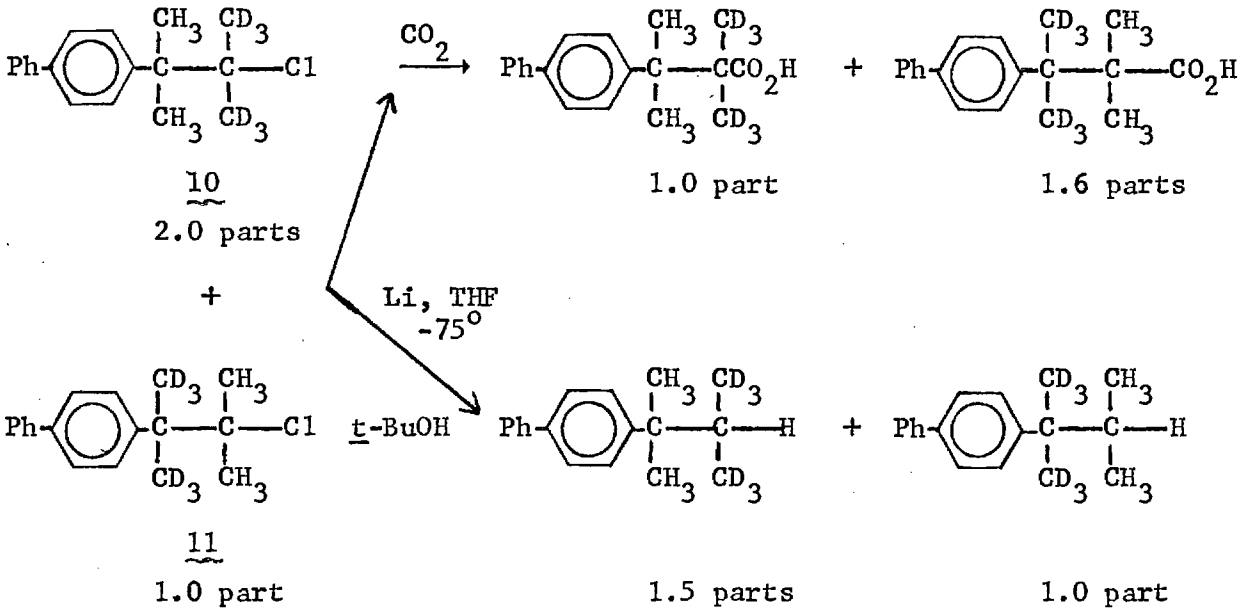
D. J. DeFrees, J. E. Bartmess, J. K. Kim, R. T. McIver, Jr., and W. J. Hehre, J. Am. Chem. Soc., 99, 6451 (1977).

Cf. W. A. Pryor, Chem. and Eng. News, June 7, 34 (1971).

Reaction of 2-p-biphenylyl-3-chloro-2,3-dimethylbutane in THF with lithium metal es only the open lithium compound 15 with no evidence for appreciable spiro anion shown by carbonation experiments which give only the acid 6. When, however, the

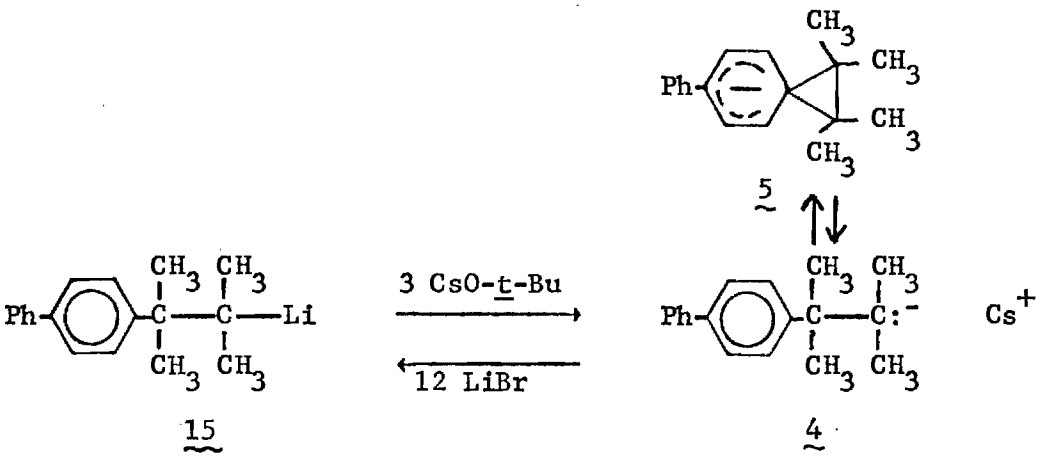


terium labeled chloride 10-11 is employed the open acid 6 has the same deuterium tribution as in reaction of the chloride with Cs-K-Na alloy. Obviously the



ganolithium compound 15 is undergoing ready [1,2] migration of the p-biphenylyl oup. That it is the carbanion (or organolithium compound) which is rearranging ther than a free radical is shown above by "trapping" experiments with tert-butyl cohol. Again carbanions are "trapped" by the alcohol prior to appreciable arrangement.

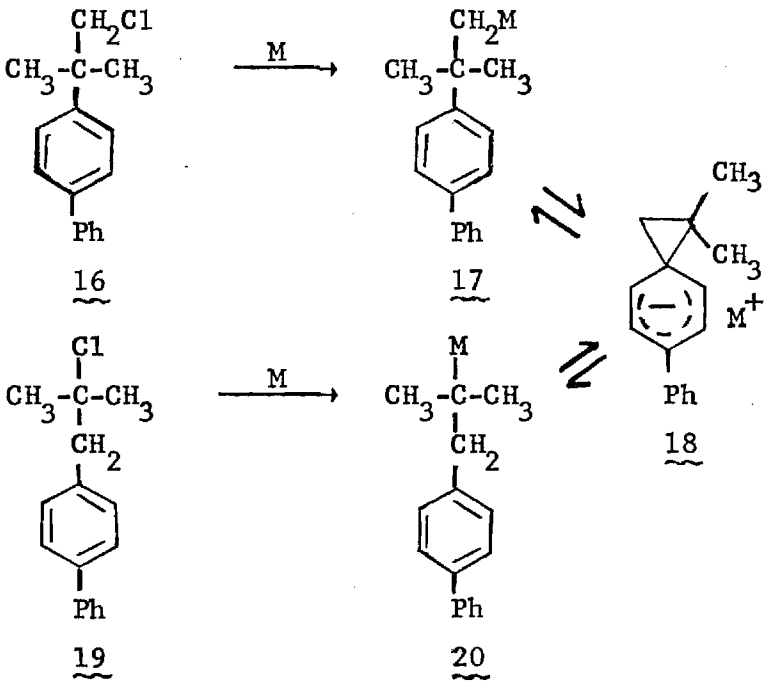
The open organolithium compound 15 serves as a convenient source of the open ganocesium compound 4 which is formed by metathesis of 15 with CsO-t-Bu in THF -75°. Since the open cesium anion 4 is in mobile equilibrium with the spiro anion cesium tert-butoxide serves as a convenient reagent to bring about spiro cyclization low temperature. Also the equilibrium mixture of 4 and 5 may be converted into the



15 4 5

n organolithium compound 15 by metathesis with LiBr in THF at -75°. These ersible changes (which are established by examination of the products of carbonation), believe, provide further and convincing evidence that the spirocyclization and [1,2] ration of p-biphenylyl is occurring in a carbanion or organoalkali compound rather n in a free radical.[6] Cation effects similar to those reported here were obtained Maercker and Roberts[6] in their study of the cyclopropylcarbinyl-homoallyl rrangement.

Our success in stabilizing the spiro anion 2 relative to the open anion 1 by two irs of gem-dimethyl groups as in 5 encouraged us to examine the "gem-dimethyl effect" Thorpe-Ingold effect[7] in greater detail in our carbanionic system. Is one set of m-dimethyl groups as in 18 adequate to stabilize the spiro anion sufficiently for tection by carbonation techniques? Does [1,2] migration of the p-biphenylyl groups ur in both of the dimethyl derivatives 17 and 20 below? To answer these questions

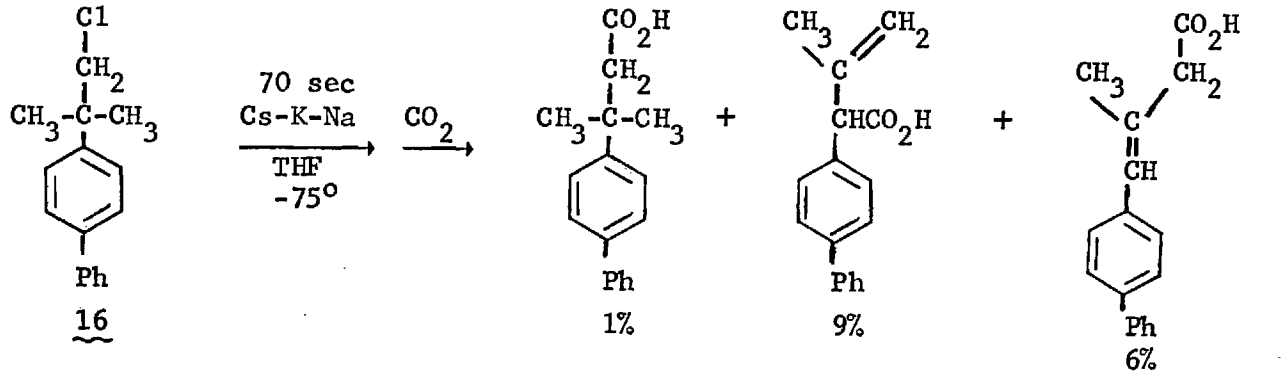


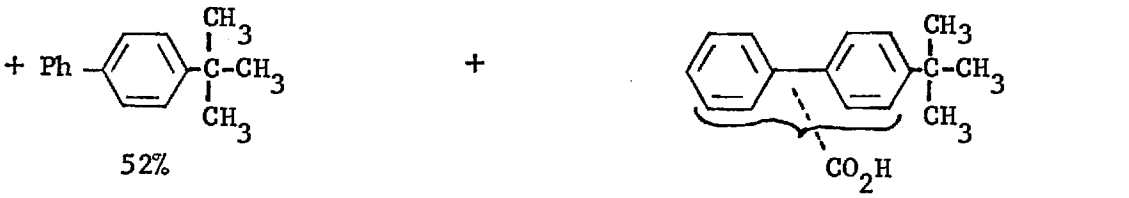
16 17 18 19 20

A. Maercker and J. D. Roberts, J. Am. Chem. Soc., 88, 1742 (1966).

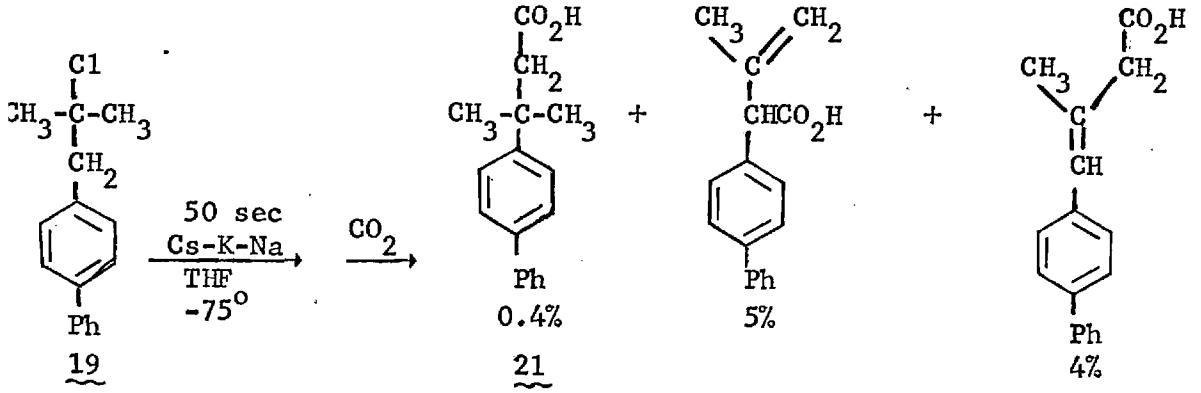
See G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N.Y., 1956. pp 460-469; B. Capon and S. P. McManus, "Neighboring Group Participation," Vol. 1, Plenum Press, New York and London, 1976, pp 58-70.

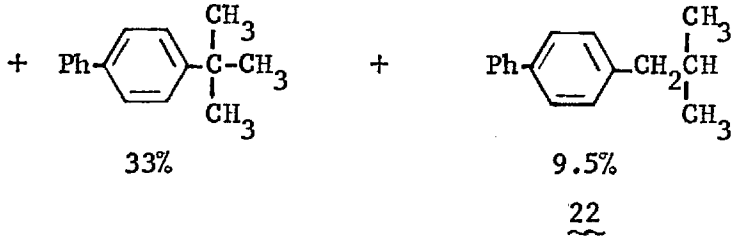
e two chlorides 16 and 19 were synthesized and allowed to react with Cs-K-Na alloy
ch the results as summarized in the schemes below.





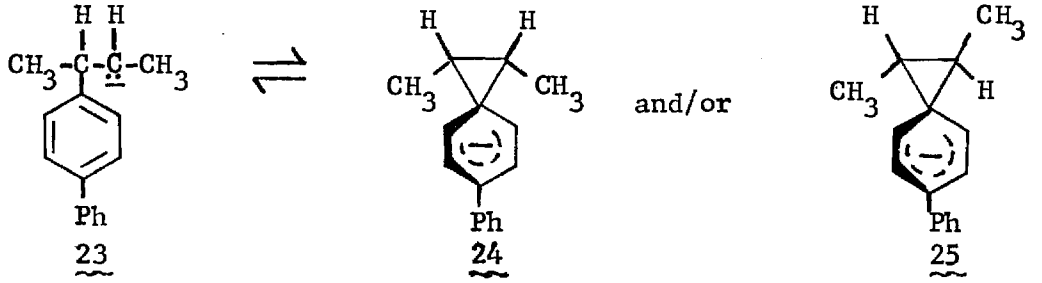
2% of various isomeric acids





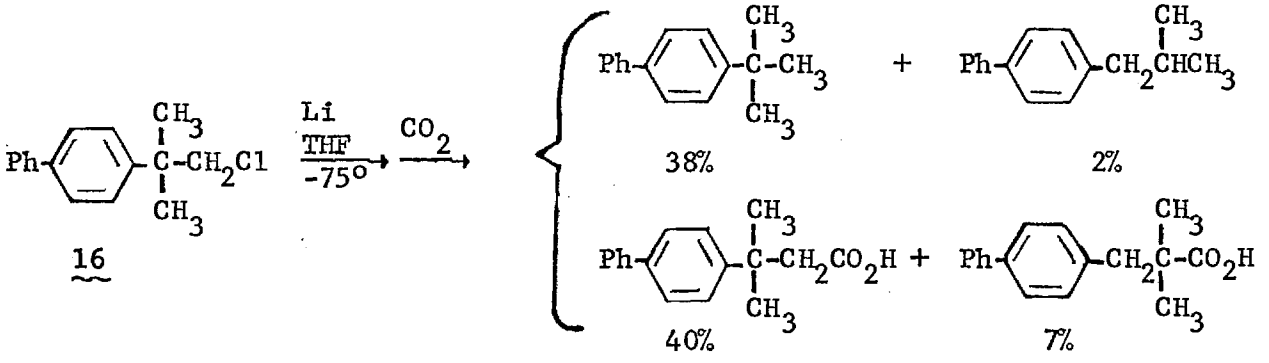
Neither chloride 16 nor 19 gave any detectable spiro carboxylic acid. While loride 16 evidently underwent α-elimination with rearrangement of the p-biphenylyl oup in a carbenoid intermediate, followed by metallation to give olefinic acids, no idence for a rearrangement of the type 17 → 18 → 20 was obtained. In contrast loride 19 gave rise to a small amount of the rearranged acid 21 and an appreciable ount of the rearranged hydrocarbon 22. Evidently the rearrangement 20 → 18 → 17 curs but not the reverse process. Most of the rearranged product 17 is protonated

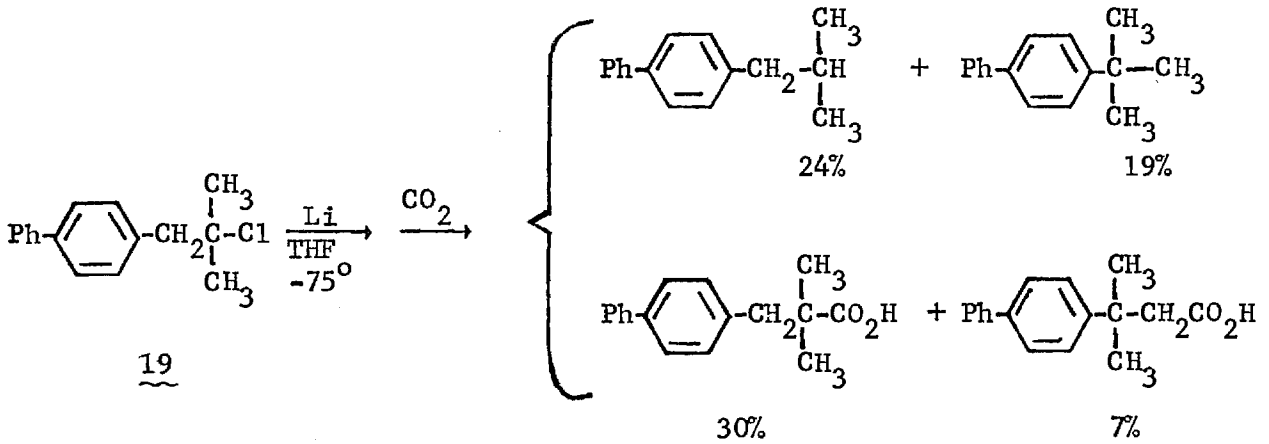
the solvent (or other acid such as the alkyl chloride) prior to carbonation. conclude that the gem-dimethyl groups in 20 facilitate rearrangement of the ganocesium compound to 17 doubtlessly via the spiro anion 18. Also the primary ganocesium compound 17 is thermodynamically more stable than either the tertiary ganocesium compound 20 or the spiro anion 18. The destablization of carbanions rganoalkali compounds) by methyl groups is rather well documented[8] for reactions liquid solution although the theoretical reason(s) for such destabilization is not ll agreed upon. Two pairs of gem-dimethyl groups as in 5 appear necessary for abilization of the spiro anion relative to open forms. It should be emphasized that, present, it is not known whether two methyl groups situated as in 24 or 25 would be



le to stablize the spiro anion relative to the open anion 23.

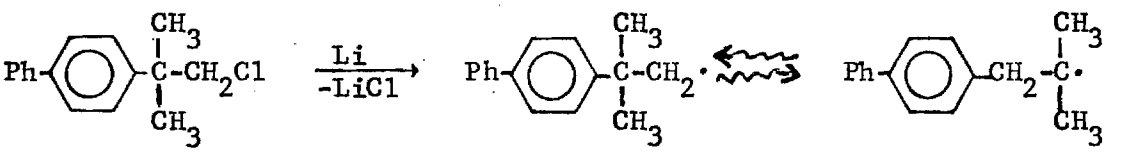
The reaction of halides 16 and 19 with lithium metal in tetrahydrofuran at -75° of interest. The results are summarized below. The amount of rearrangement for





D. J.Cram, "Fundamentals of Carbanion Chemistry," Academic Press, Inc., N.Y., N.Y., 1965, Chapter I.

action of halides 16 and 19 with lithium did not increae with increase in reaction ne nor did the amount of rearrangement from halide 16 increase with increase in action temperature as shown by analyses for the volatile products listed in the ove reaction summaries. Also when the reactions of halides 16 and 19 with lithium e run in THF containing a little tert-butyl alcohol the amount of rearrangement s not appreciably reduced. The organolithium compounds from chlorides 16 and 19 NOT rearrange upon standing and the rearrangements observed are NOT rearrangements carbanions but evidently rearrangements of free radicals formed during reaction the lithium surface, e.g.



ier examples of rearrangements of radicals during reactions of organic chlorides with thium metal have been reported[9] from our laboratories.

[1,2] Migration of Phenyl during Preparation of Grignard Reagents

In experiments directed toward preparation of an authentic sample of acid for use a standard in the analysis of products from rearrangement of an organoalkali metal mpound, we discovered that a phenyl group migrates partially during the preparation of e Grignard reagent from 5-chloro-4,4-diphenyl-1-pentene. In fairly extended studies enyl groups were also found to under [1,2] migration during preparation of Grignard agents from 2-chloro-1,1,1-triphenylethane and 1-chloro-2,3,4-triphenylpropane. The ignard reagent itself once prepared from these halides does not undergo detectable arrangement. The observed phenyl migration, therefore, occurs during formation of e Grignard reagent, likely by way of radicals formed at the surface of the magnesium tal just as we have observed for reactions of chlorides with lithium metals. Our sults on phenyl migration during preparation of Grignard reagents have now been blished in detail[10].

[1,2] Migrations of Phenyl and Acetylene Groups in Reactions of 1-Chloro-5,5-dimethyl-2-diphenyl-3-pentyne and 5-Chloro-4,4-diphenyl-2-pentyne with Alkali Metals

While [1,2] rearrangements of vinyl groups in organoalkali compounds and Grignard agents have been known for some time, apparently only one example of migration an acetylene group in a Grignard reagent has been reported.[11] We have und that 5-chloro-4,4-diphenyl-2-pentyne (26) reacts with lithium metal -78° to give the expected organolithium product 27 which undergoes

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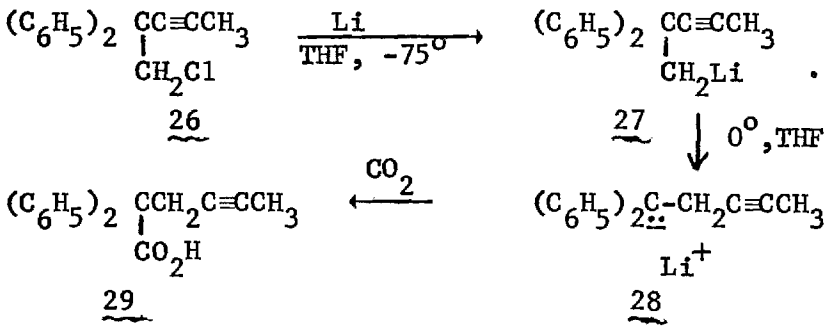
E. Grovenstein and Y.-M. Cheng, Chem. Commun., 101 (1970); E. Grovenstein, Jr., and J.-U. Rhee, J. Am. Chem. Soc., 97, 769 (1975).

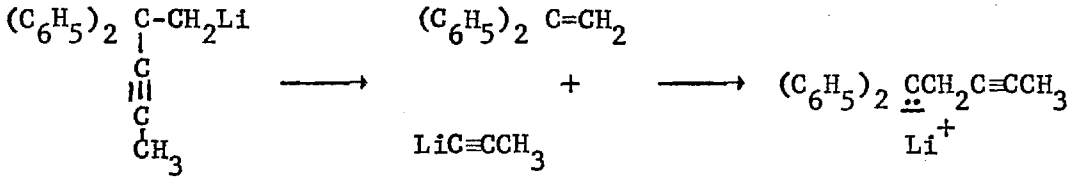
E. Grovenstein, Jr., A. B. Cottingham, and L. T. Gelbaum, J. Org. Chem., 43, 3332 (1978).

E. Grovenstein, Jr., Angew. Chem. Int. Ed. Eng., 17, pp 320-323 (1978); E. A. Hill, J. Organometal. Chem., 91, 123-271 (1975).

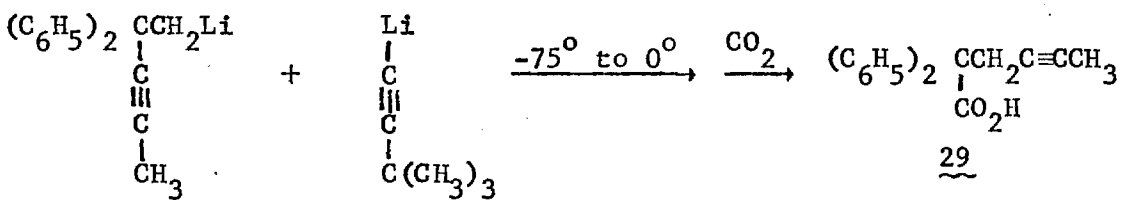


,2] migration of the $-C\equiv CCH_3$ group upon warming to 0° to give 28 which was aracterized by carbonation to yield 29.

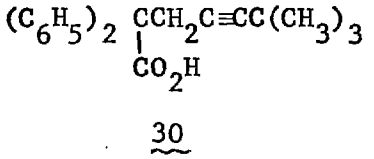
One possible mechanism for rearrangement of 27 would be by an elimination-readdition ocess outlined below:



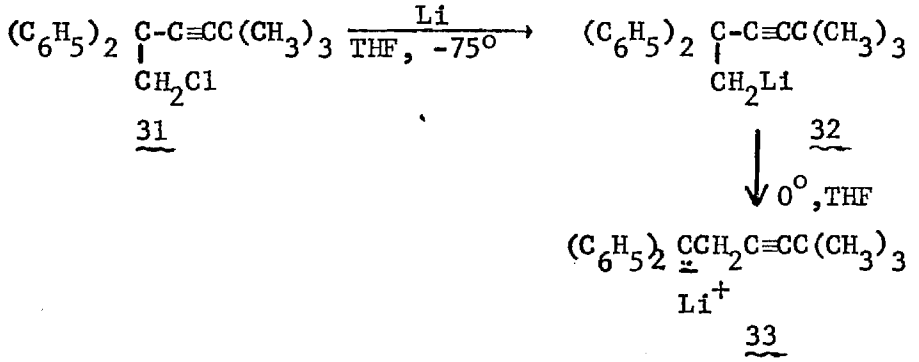
the above mechanism were valid, it should be possible to intercept the intermediate henylethylene with another organolithium reagent such as $LiC\equiv CC(CH_3)_3$. Hence the st below has been carried out:



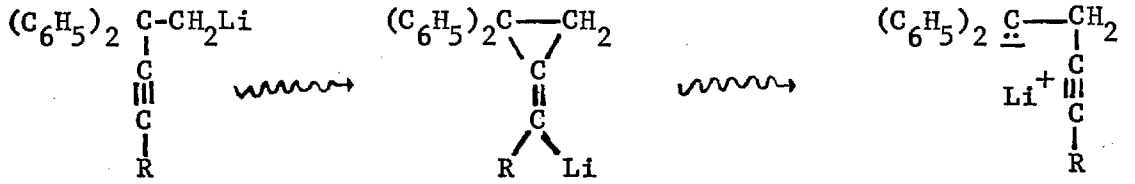
wever, only the usual rearrangement product 29 was obtained and none (<1%) of the utylacetylene-incorporation product 30 could be detected.



That indeed a t-butylacetylene group is able to under a [1,2] rearrangement like e methylacetylene group of 27 was demonstrated by preparation and rearrangement of to 33 under conditions analogous to those used for 27.

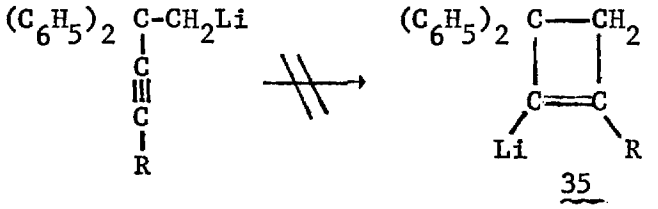


The most likely mechanism for the observed [1,2] migration of the acetylene ›ups in our organolithium compounds is by way of intermediate 34. This mechanism is



34

ılogous to that accepted for migration of vinyl and aryl groups; however, the ring ›sure to 34 is an example of an 3-exo-digonal process which is disfavored by Baldwin's les[12]. These rules would favor instead the 4-endo-digonal ring closure to 35 which, ‹ever, would not appear capable of leading to the observed products 28 and 33.

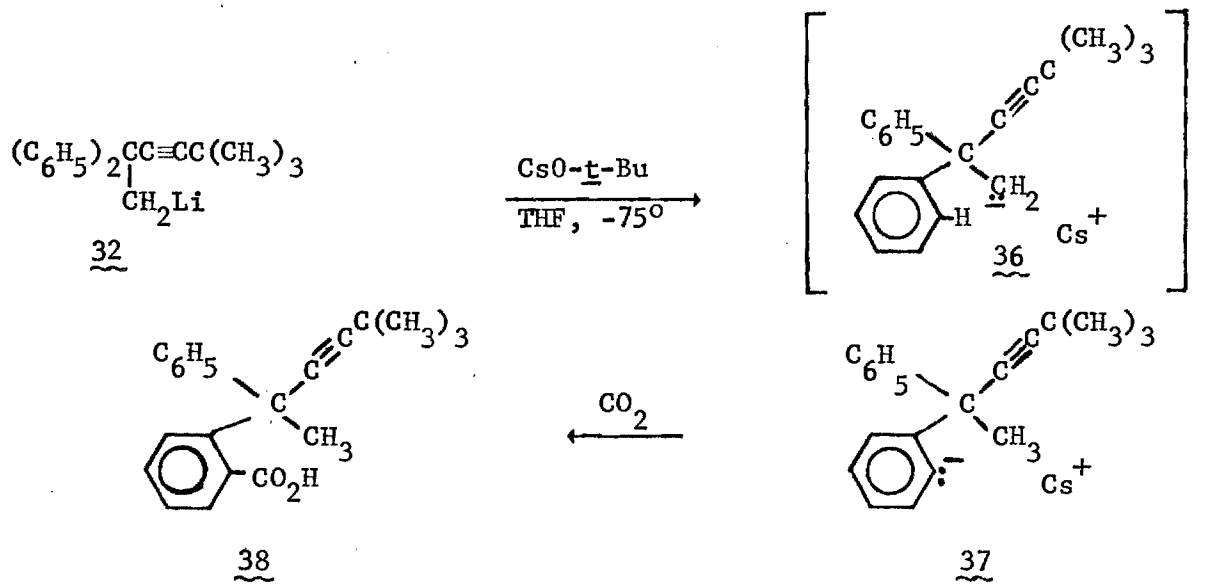


35

To probe the role played by the lithium cation in the above rearrangements of ɛtylene groups the organolithium compound 32 was treated with CsO-t-Bu at -75° with ɛ aim of making the corresponding organocesium compound according to the general tathetical process shown in the following equation:

$$RLi + CsO\text{-}t\text{-}Bu \rightarrow RCs + LiO\text{-}t\text{-}Bu$$

fact CsO-t-Bu catalyzed a new rearrangement of 32 evidently to the ortho metallation ›duct 37. The structure of 37 rests upon the spectroscopic properties of its product of

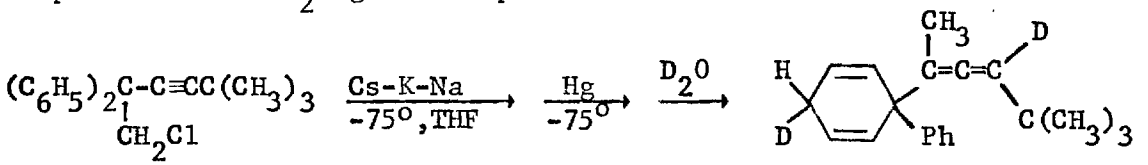


32 36 38 37

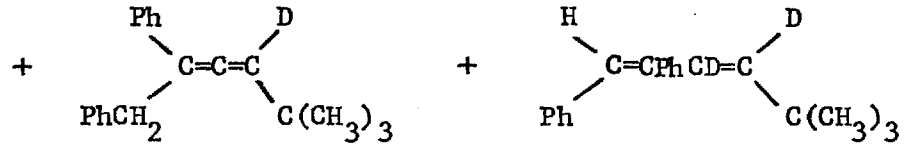
J. E. Baldwin, J. Chem. Soc. Chem. Comm., 734 (1976).

:bonation 38; while the structure of 38 is likely correct, in view of some results :h Cs-K-Na alloy described below, it needs confirmation.

The putative organocesium compound 36 was made also by reaction of the corresponding loride 31 with Cs-K-Na alloy at -75°; treatment with mercury to remove excess alloy l decomposition with D_2O gave the products shown below.



31 39

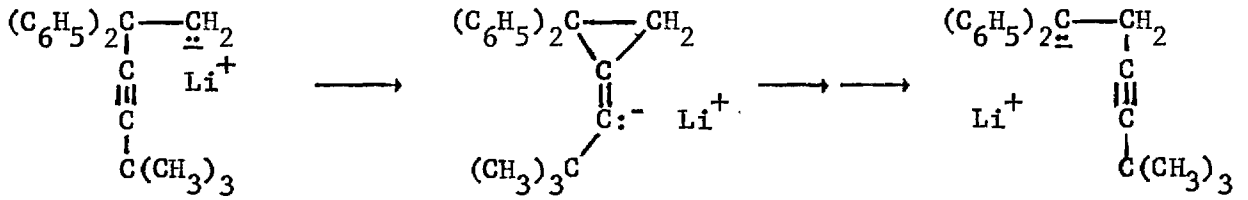


40 41

e ratio of 39:40:41 was approximately 40:30:30.

The products 39-41 may be accounted for by Scheme 1 (see page 12a). The organocesium mpound 42 is given the same structure as that 36 formed by way of the corresponding ganolithium compound 32. Yet 42 and 36 give different products! This is explained the basis that 36 is formed initially as a solvent separated or loose ion pair; erefore, 36 is highly reactive and stabilizes itself by interaction with the nearest lic proton which happens to be one in an ortho position of the two neighboring phenyl oups. Organocesium compound 42 formed by reaction of the chloride 31 with cesium loy is evidently formed initially as a tight ion pair (contact ion pair). Species is therefore longer lived than 36 and survives long enough to under [1,2] gration of the phenyl group or to extract a proton from anion 43 or from the solvent. is notable that whereas the organolithium compound 32 undergoes only [1,2] migration the acetylene group, the organocesium compound 42 undergoes only [1,2] gration of the phenyl group. That cesium as counter cation nds to favor migration of phenyl over other groups relative to lithium as counter tion has now been demonstrated in three cases: phenyl versus benzyl migration[13], enyl versus allyl migration[14], and the present phenyl versus acetylene migration.

Our explanation for the cation effect upon the present rearrangements is that ganolithium compound 32 rearranges in a tight ion pair via species 51 and 52 to e delocalized product 53. The reason why the tight ion pair with lithium (51)

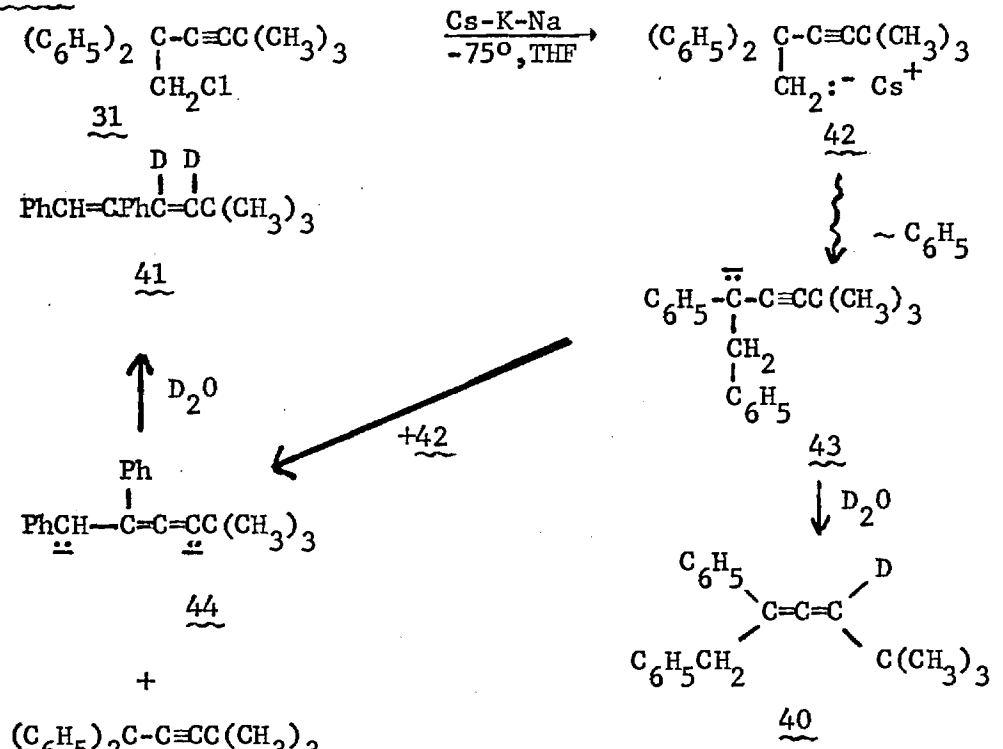


51 52 53

E. Grovenstein, Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975).

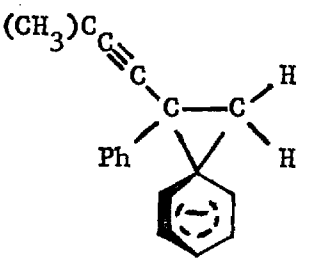
E. Grovenstein, Jr., and A. B. Cottingham, J. Am. Chem. Soc., 99, 1881 (1977).

ıeme 1



12a

es migration of the acetylene group whereas the tight ion pair with cesium
) gives migration of the phenyl group depends upon the fact that
hium cation has an ionic radius (0.60Å) about the size of the covalent radius of
bon (0.77Å) whereas cesium cation has an ionic radius (1.69Å) about the size of
radius of a benzene ring (1.40Å for the ring of carbon nuclei). The net result of
trostatic and covalent forces of attraction between these alkali metal cations
their gegen anions appears to be that small lithium cations interact better with
alized anions as in 51 and 52 than with delocalized anions such as 54 (which



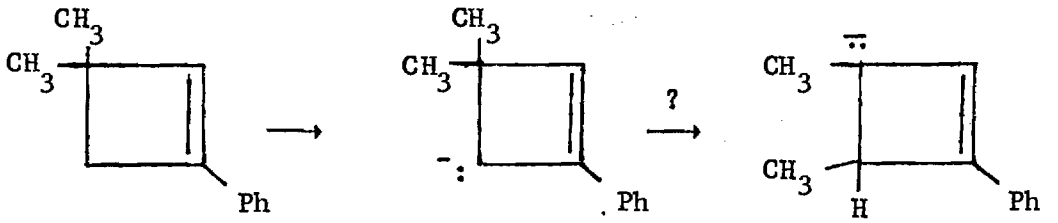
54

the intermediate or transition state for phenyl migration) whereas large
ium cations interact better with the large delocalized anion 54 than with the
alized anionic charge of 51 and 52.

The origin of product 39 as shown in Scheme 1 is discussed in Part II,
actions of Cesium and Cesium Alloys with Aromatic Hydrocarbons."

Search for [1,2] Migration of Methyl in Cyclobutenyl Anions

Previous unpublished work in our laboratory had as its goal study of possible [1,2]
gration of methyl in the anion 56 whose synthesis was sought via reaction of olefin 55
h strong bases. This goal was frustrated by various alternative reactions, addition

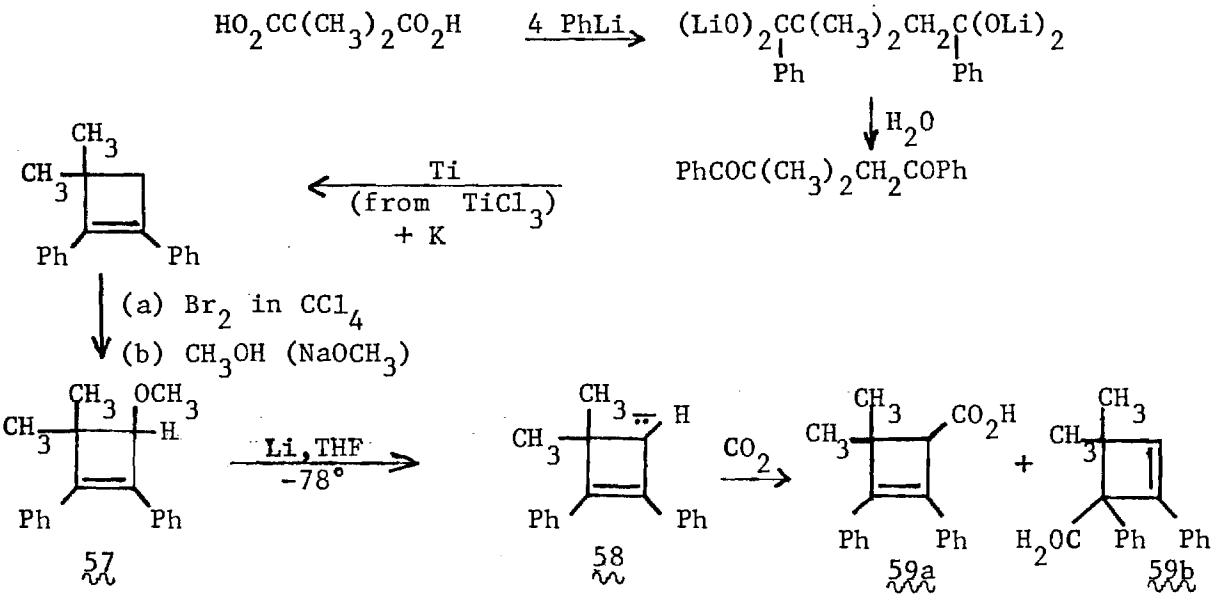


55 56

the base (e.g. n-butyllithium + tetramethylethylenediamine to the olefinic bond and
ssible metallation of the vinylic position or the aromatic ring of 55.

E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, J. Org. Chem., 37, 1281 (1972).

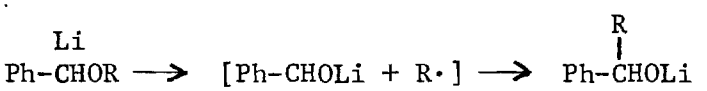
In new work the vinylic hydrogen of 55 has been replaced by a phenyl group which should h make vinylic metallation impossible and increase the stability of the allylic anion 56. o the allylic anion has been sought by ether cleavage of 57 with alkali metals rather n by metallation. The following synthesis of 58 has been successfully achieved.



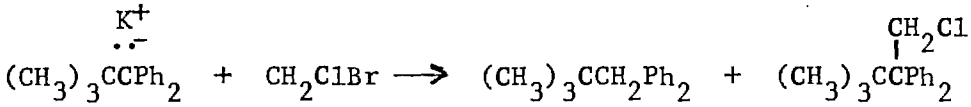
The mixture of carboxylic acids from carbonation of the carbanion, both after its paration at -78°C and after warming to 0° for three hours, has been shown to contain , likely 59b, and compounds of longer GC retention time (possibly dicarboxylic acids, ymers and/or their pyrolysis products). Full identification is complicated by thermal tability of 59a and 59b; however, the results to date suggest that methyl migration 58 is NOT a facile process.

Search for [1,2] Migration of tert-Butyl in 2,2-Diphenyl-3,3-dimethylbutyl Anion

Lansbury, Schöllkopf, and coworkers[16] have suggested that the Wittig rearrangement of ers proceeds via dissociation into a radical pair:



o it was noted that a tert-butyl group migrated 2080 times more readily than a methyl up in lithiobenzyl alkyl ethers. The ready migration of tert-alkyl groups in Wittig er rearrangements suggested the desirability of looking for corresponding migrations simpler carbanions without heteroatoms. Hence we have studied the rearrangement of -diphenyl-3,3-dimethylbutyllithium. The synthesis of this compound posed some experi- tal difficulties. The usual synthesis by reaction of the corresponding chloride with hium metal was made impossible by the unavailability of the pure chloride. Attempts make the chloride by reaction of 2,2-dimethyl-1,1-diphenylpropyl anion (60) with



60 61 62

her dichloromethane or bromochloromethane gave mostly the hydrocarbon 61 and little the desired chloride 62. Efforts to separate 62 from 61 by chromatography on silica

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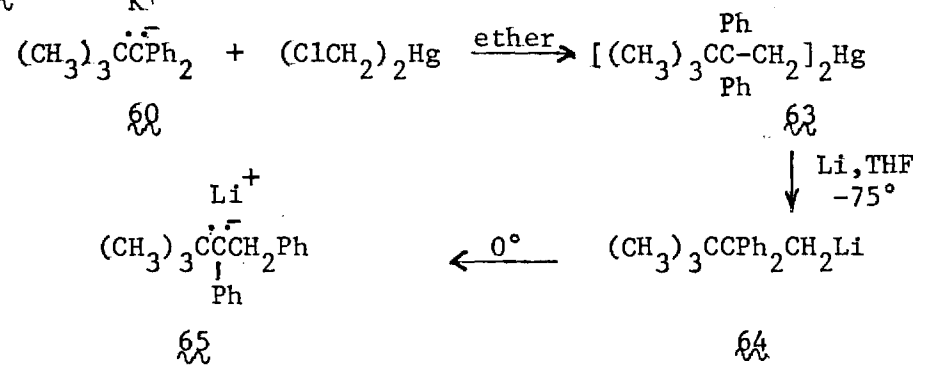
P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, J. Am. Chem. Soc., 88, 78 (1966); V. Schöllkopf, Angew. Chem. Int. Ed. Eng., 9, 763 (1970).

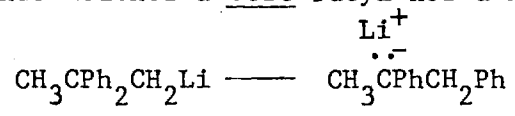
were vitiated by decomposition of 62 (evidently both steric acceleration and
ıyl participation in 62 make this halide unusually reactive via mechanism S_N1).
ɔessful synthesis of 2,2-diphenyl-3,3-dimethylbutyllithium was finally accomplished
Scheme 2 which utilizes the novel reaction of the anion 60 with bis(chloromethyl)-

eme 2



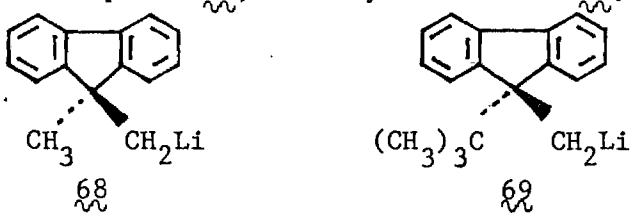
60 63 64 65

ɔury to give the product of S_N2 displacement on carbon 63 and negligible amounts of
hydrocarbon 61. The organolithium compound 64 when warmed to 0° in THF underwent
2] migration of phenyl and no observable migration of tert-butyl just as the methyl
log 66, according to Zimmerman and Zweig,[17] underwent phenyl migration without observable
hyl migration. Thus neither a tert-butyl nor a methyl group has sufficient migratory



66 67

itude to compete with phenyl in rearrangement of these organolithium compounds without
eroatoms. This is of course not to say that, if migration of the phenyl group could be
arded, migration of tert-butyl would be unobservable. For example, Eisch and Kovacs[18]
nd that organolithium compound 68, closely related to 66, underwent neither migration of



68 69

yl nor methyl; evidently aryl migration in 68 involves (for the usual, low energy
thway) a highly strained spiro intermediate or transition state. Hence, in absence
aryl migration, tert-butyl migration may yet be observable in 69.

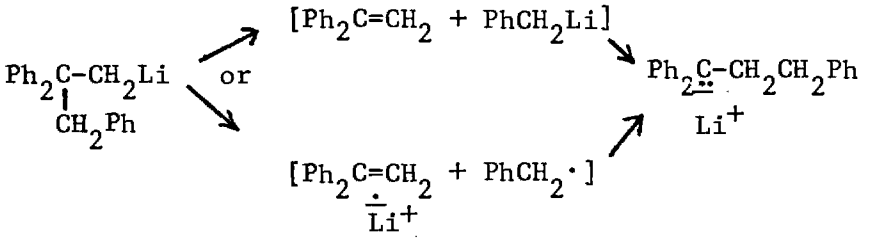
Rearrangement of 2,2-Diphenyl-3-p-tolylpropyl Anion

While the rearrangement of benzyl in 2,2,3-triphenylpropyllithium is most simply
plained as proceeding via an elimination and readdition of benzyllithium, Grovenstein
d Wentworth[19] pointed out that this rearrangement could proceed via cleavage to a
dical pair as has been suggested for Wittig ether rearrangements[16]:

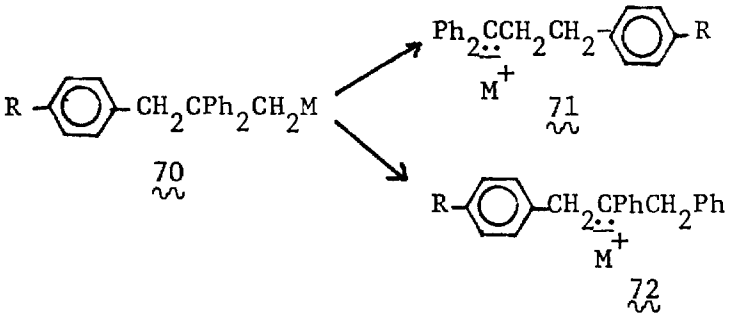
H. E. Zimmerman and A. Zweig, J. Am. Chem. Soc., 83, 1196 (1961).

J. J. Eisch and C. A. Kovacs, J. Organomet. Chem. 25, C33 (1970).

E. Grovenstein, Jr., and G. Wentworth, J. Am. Chem. Soc., 85, 3305 (1963); ibid, 89, 1852 (1967).



nce subsequent work[20] showed that the 2,2,3-triphenylpropyl anion can (under appropriate nditions) undergo competitive migration of phenyl via a concerted process, a method s now apparent to distinguish between the two possible fragmentation processes. Namely, a para substituent is placed in the benzyl group, it should be possible to accelerate retard the migration of benzyl relative to phenyl dependent upon whether the group abilizes or destabilizes anions versus radicals. A para methyl group should retard rmation of the benzyl anion[21] but accelerate somewhat formation of the benzyl radical[22] ile leaving the rate of phenyl migration nearly unaffected. The results from our periments are recorded below.



Relative Yields

M	Temp., °C	R = H[20] 71:72	R = CH_3 71:72
Li	0°	99:<1	99:<1
K	-75°	63:37	25:75
Cs	-75°	25:75	<1:99

The results show that rearrangement of the compound with a para methyl group rallels that of the unsubstituted compound; but that in every case in which the ratio 71 to 72 is measurable, it is smaller for the compound with the para methyl bstituent. In other words the para methyl substituent has reduced the amount of nzyl migration relative to phenyl migration. The results are therefore in agreement th benzyl migration occurring by elimination and readdition of benzyl anion rather than nzyl radical. Also the results continue to demonstrate an interesting cation effect[20] rearrangement of 70. The large difference in the ratio of 71 to 72 even on going from tassium to cesium is notable and stresses that the organometallic chemistry of cesium y frequently be different in a synthetically useful manner from that of the other kali metals.

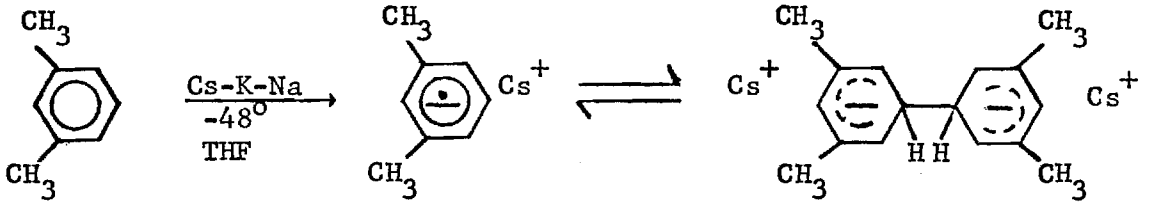
) E. Grovenstein, Jr., and R. E. Williamson, J. Am. Chem. Soc., 97, 646 (1975).

G. Gau and S. Marque, J. Am. Chem. Soc., 98, 1538 (1976); A. Streitwieser, Jr., and J. H. Hainmons, Prog. Phy. Org. Chem., 3, 59-65 (1965).

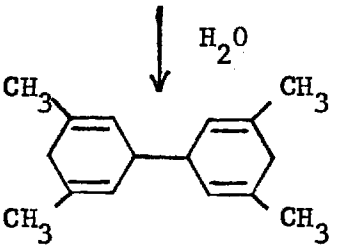
W. A. Pryor, "Free Radicals," McGraw-Hill Co., New York, 1966, pp 169, 173, and 175; C. Rüchardt, Angew. Chem. Int. Ed. Eng., 9, 830 (1970); S. Dinctürk, R. A. Jackson, and M. Townsend, J. C. S. Chem. Comm., 172 (1979).

RT II. Reactions of Cesium and Cesium Alloys with Aromatic Hydrocarbons

Our work upon reaction of cesium and Cs-K-Na alloy with benzene and toluene has w been published[23] and, therefore, will not be discussed further here. In similar nner m-xylene reacts with excess Cs-K-Na alloy in THF at -48° to give the radical ion 73 which largely dimerizes to 74 as judged by the dimeric hydrocarbon 75 which obtained in 55% yield as a beautifully crystalline compound upon siphoning the action mixture into ice water.

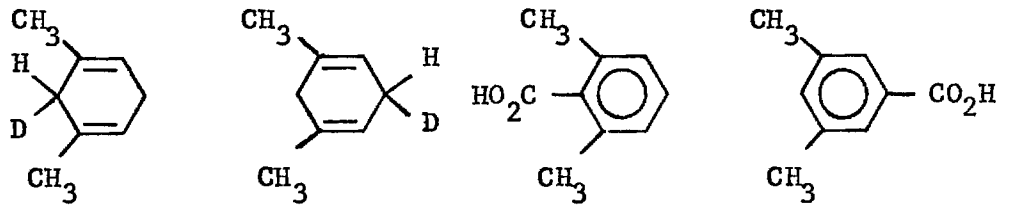


73 74



75

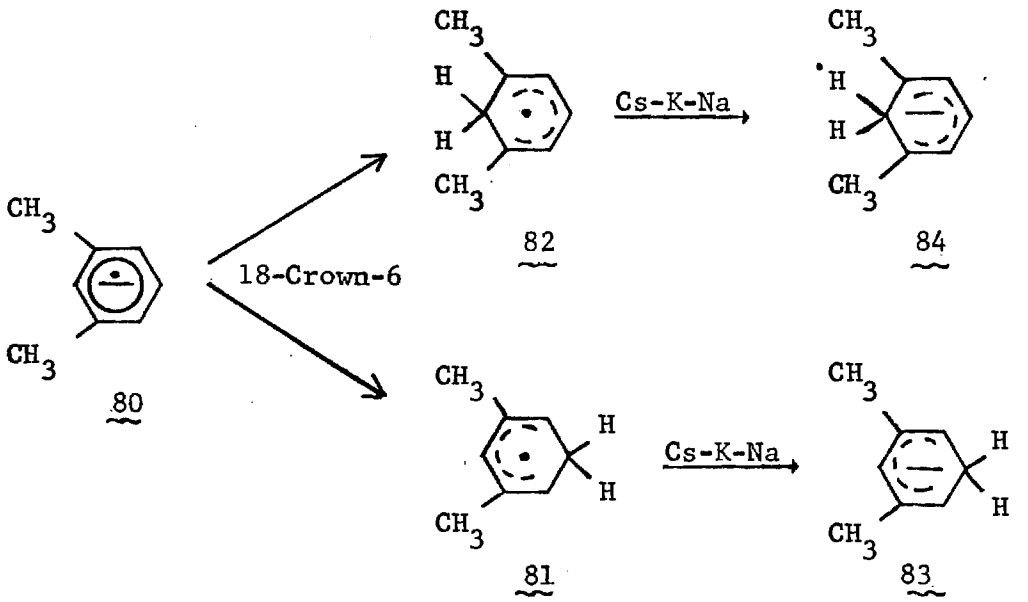
In contrast reaction of m-xylene with Cs-K-Na alloy in THF in presence of one lar equivalent of 18-crown-6 gave on protonation after some three hours only nomeric hydrocarbons. For a reaction which was quenched with D_2O, 64 mole % of 5-dihydro-m-xylene and 33 mole % of unreacted m-xylene was obtained. According ^1H and ^{13}C NMR analysis, the 2,5-dihydro-m-xylene was monodeuterated and consisted a 1 : 3.74 ratio of 76 to 77. In another run with two molar equivalents of -crown-6 per mole of m-xylene, the acidic product from carbonation and dehydrogenation nsisted of a 1: 3.86 ratio of 78 to 79. These data are in good argeement with the



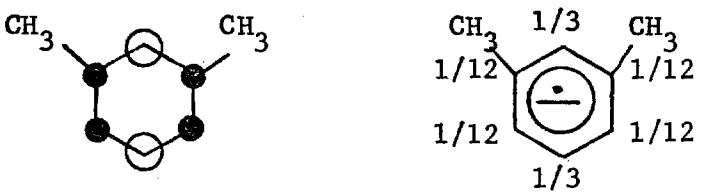
76 77 78 79

nclusion that 18-crown-6 protonates the radical anion 73 to give about a 1 : 3.8 xture of radicals 81:82 which are reduced to the corresponding ratio of anions 83 : 84.

E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Am. Chem. Soc., 99, 2800 (1977).



Note that the chemistry of m-xylene radical anion can be interpreted in terms of e HOMO structure 85 or the charge distribution 86[24]. Dimerization and protonation



85 86

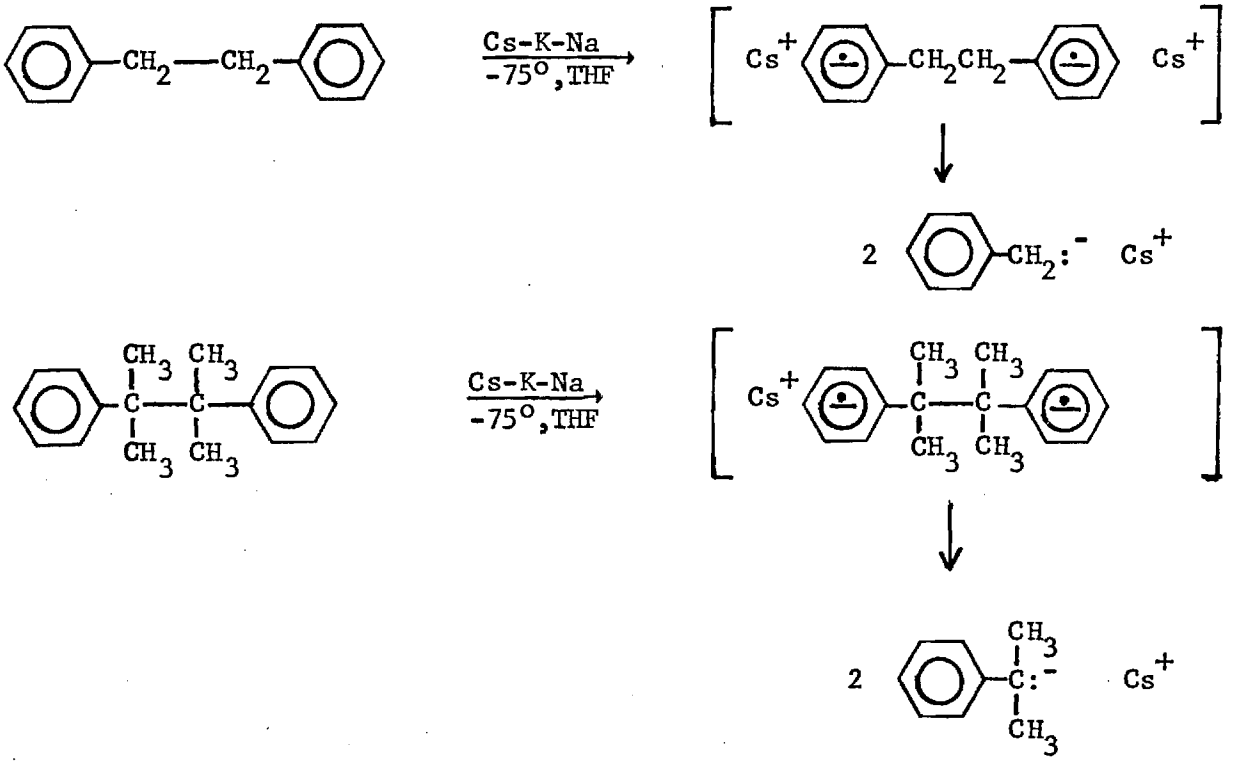
the radical anion would be expected to take place at the positions of highest electron-in density or charge density, hence at positions 2 or 5. Dimerization takes place eferentially at the 5 positiion since this process leads to the most stable anion 74 ere the methyl groups are at the nodal positions in the HOMO (and hence destabilize e anions as little as possible). Protonation in contrast occurs preferentially at e 2-position since this process leads to the most stable radical 82 where the methyl oups are all at centers of high spin density (and hence stabilize the radical as ch as possible). The higher regiospecificity in dimerization than in protonation cords with the larger effect of methyl groups in destabilizing anions than in abilizing radicals in solution. The theoretical explanation of this substituent fect is poorly understood but the effect is of considerable importance to free dical and carbanion chemistry.

In similar experiments with benzene and Cs-K-Na alloy in THF at -43° in presence two molar equivalents of 18-crown-6 for five hours, the products of carbonation dicated that somewhat less than half of the benzene radical anion was protonated 18-crown-6 in contrast to complete protonation of m-xylene radical anion under

[24] See L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, N. Y., N. Y., 1966, p. 255.

lder conditions. These comparative results may be understood on the basis that thyl groups destabilize radical anions and increase their rate of protonation 18-crown-6.

The cleavage reactions shown below have been observed to take place readily at w temperature likely by way of intermediate dianions. The yields of benzylic anions



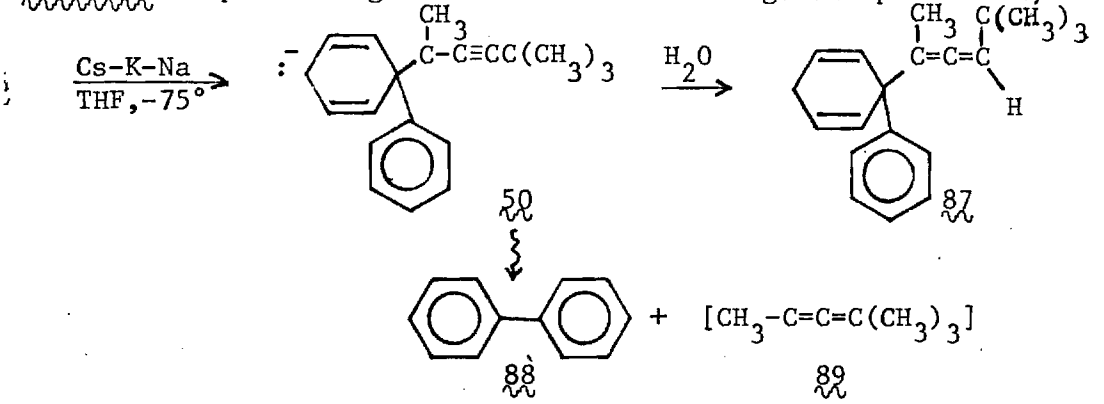
:e quantitative. These reactions would appear to be of synthetic utility.

Experiments on the reaction of 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (31) with

$$ClCH_2C(Ph_2C{\equiv}CC(CH_3)_3 \longrightarrow CH_3C(Ph_2)C{\equiv}CC(CH_3)_3$$

31 46

-K-Na alloy in THF at -75° suggested that 31 was partially converted to the hydrocarbon which reacted with excess Cs-K-Na alloy according to the processes shown in detail Scheme 1 on p 12a to give the unusual rearrangement product 50. This suggestion has



ow been confirmed by subjecting the hydrocarbon 46 to the reaction conditions of the ıloride 31 and obtaining a hydrocarbon 87 identical to that obtained from the chloride.

addition biphenyl (88) accompanied the formation of 87 and may readily be
terpreted as arising from fragmentation of anion 50 which is the precursor of 87.
e rearrangement of the hydrocarbon 46 to the anion 50 is to our knowledge without
ecedent. This rearrangement is a good example of the powerful reducing potential
cesium alloy and of the unique chemistry which cesium provides at very low reaction
mperatures.